PB-223 622

IMPACT ON MAN OF ENVIRONMENTAL CONTAMINATION CAUSED BY LEAD

H. W. Edwards, et al

Colorado State University

Prepared for:

National Science Foundation

July 1971

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 223 622

IMPACT ON MAN OF ENVIRONMENTAL CONTAMINATION CAUSED BY LEAD

NSF GRANT GI-4

INTERIM REPORT
JULY 1, 1970 to JUNE 30, 1971

H. W. EDWARDS
PRINCIPAL INVESTIGATOR

COLORADO STATE UNIVERSITY
FORT COLLINS, COLORADO

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
US Department of Commerce
Springfield, VA. 22151

BIBLIOGRAPHIC DATA SHEET

1. Report No. NSF/RA/E-72-003
2.
3. Recipient's Accession No. PB-223 622
4. Title and Subtitle
Impact on Man of Environmental Contamination Caused by Lead
5. Report Date
July, 1971
6.
7. Author(s)
H. W. Edwards, et al.
8. Performing Organization Rept. No.
9. Performing Organization Name and Address
Colorado State University
Fort Collins, Colorado
10. Project/Task/Work Unit No.
11. Contract/Grant No.
GI-4
12. Sponsoring Organization Name and Address
National Science Foundation
Division of Environmental Systems and Resources
Washington, D.C. 20550
13. Type of Report & Period Covered
Progress Report
7/1/70 to 6/30/71
14.
15. Supplementary Notes
16. Abstracts

Objectives of research at CSU by interdisciplinary team are: (1) to develop and test an interdisciplinary approach to environmental problems using lead as an example; and (2) to evaluate consequences of lead pollution from traffic exhaust and economic and technological effects of steps taken to reduce lead pollution from this source. Emphasis during the phase of the program covered in this report is upon pilot experiments to determine where, in what forms, and at what rate lead from traffic exhaust is accumulating in the environment.

17. Key Words and Document Analysis. 17a. Descriptors

1302	Pollution
0702	Lead Inorganic Compounds
0703	Lead Organic Compounds
0606	Ecology

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group

0606	Environmental Biology
04	Atmospheric Sciences

18. Availability Statement
19. Security Class (This Report) UNCLASSIFIED
20. Security Class (This Page) UNCLASSIFIED
21. No. of Pages ~~169~~ 180
22. Price $11.00/1.45

ia

FORM NTIS-35 (REV. 3-72)

THIS FORM MAY BE REPRODUCED

USCOMM-DC 14952-P72

IMPACT ON MAN OF ENVIRONMENTAL CONTAMINATION CAUSED BY LEAD

Interim Report

for the period

July 1, 1970 to June 30, 1971

by

H. W. Edwards

and

M. L. Corrin
L. O. Grant
L. M. Hartman
E. R. Reiter
R. K. Skogerboe
C. G. Wilber
R. L. Zimdahl

COLORADO STATE UNIVERSITY

FORT COLLINS, COLORADO

Supported by

National Science Foundation
Grant GI-4

TABLE OF CONTENTS

I. Summary 1

- General 1
- Atmospheric Transport 1
- Cloud Chamber Tests 2
- Possible Inadvertent Cloud Seeding 2
- Accumulation of Lead in Animals 3
- Lead in Soil 3
- Economic Aspects 3
- Chemical Analysis 3
- Transport Model 4
- User Groups 4
- Interdisciplinary Team Approach 4

II. Background 6

III. Objectives and Approach 16

- A. Introduction 16
- B. Objectives 16
- C. Interdisciplinary Approach 20
- D. Group Meetings 25
- E. Interaction with User Groups 28
  - 1. Three-University Lead Study 28
  - 2. National 31
  - 3. Symposium on Interdisciplinary Research 32
  - 4. Industry 32
  - 5. State and Local 33
  - 6. Colorado State University 34
  - 7. Project Papers 35

IV. Atmospheric Transport of Lead 38

- A. Introduction 38
- B. Meteorological Measurements and Air Sampling 41

- C. Instrumentation and Meteorological Measurements 42
  - 1. Bivane Anemometers 42
  - 2. Platinum Resistance Thermometry 45
  - 3. Recording Equipment 45
  - 4. Mobile Units 53
  - 5. Preliminary I-25 Results 56
- D. Site Selection 57

V. Atmosperic Chemistry 62
- A. Introduction 62
- B. Air Sampling 62
- C. Gaseous Tracer 65
- D. Characterization of PbBrCl 66
- E. Solubility of PbBrCl in Water 68
- F. Electrostatic Experiments 73
- G. Exhaust Filter 74
- H. Low-Lead Water 74
- I. Particle Size Distribution 74

VI. Inadvertent Weather Modification 77
- A. Introduction 77
- B. Nucleation Activity of Leaded and Unleaded Exhaust 78
- C. Background Nucleation Activity at Climax, Colorado 82
- D. Activation Spectra for Automotive Exhaust 84
- E. Continuing Work 87

VII. Bioaccumulation of Lead 89
- A. Introduction 89
- B. Lead Uptake in Mice 90
- C. Autopsy Data 92
- D. Microbial Systems 92

VIII. Lead in Soil and Plants 93
A. Introduction 93
B. Site Selection 94
C. Field Measurements
1. Background Lead in Soil 95
2. Lead in Roadside Soil 95
D. Radiotracer Experiments 99
E. Rate of Immobilization 99
F. Equilibrium Immobilization Study 101
G. Column Leaching Studies 101
H. Surface Area, Cation Exchange Capacity 106
I. Lead in Plants 106

IX. Transport Model 109
A. Introduction 109
B. Conceptual Model 110
C. Analytical Formulation 116
1. Atmospheric Transport 119
2. Current Status 119

X. Economic Aspects of Lead 121
A. Introduction 121
B. Production of Lead Antiknock Compounds 122
C. Input-Output Analysis 127
1. Mechanics of the Input-Output Model 127
2. Analysis 129
D. Benefits 135
E. Societal Action 138

XI. Central Analytical Service 142
A. Introduction 142
B. Soil Samples 143
1. Emission Spectroscopy 143
2. Atomic Absorption 148

        3. Comparison of AAS and Emission Techniques 150
        4. Lead Compound Characterization 153
    C. Air Filter Analysis 154
        1. Effect of Silica 155
        2. Volatilization of Lead 158
    D. Biological Samples 159
    E. Compound Identification 160
    F. Isotope Ratio Analysis 160

XII. References 161

LIST OF TABLES

I. Industrial Lead Consumption in the United States 7

II. Arguments Against Lead in Gasoline 8

III. Arguments for Lead in Gasoline 10

IV. Colorado State University Environmental Lead Project Research Participants 21

V. Analysis of Equipment Checkout Data 46

VI. Partial Preliminary Printout of Millivolt Data 50

VII. Partial Preliminary Printout of Millivolt Data as Recorded on Magnetic Tape 51

VIII. Partial Printout of Data Converted into Engineering Units and Degrees 52

IX. Interplanar Spacing Values for PbBrCl 66

X. Solubility of PbBrCl in Water 68

XI. Stability Calculations for PbBrCl 72

XII. Numbers of Ice-Producing Nuclei per Liter in Leaded and Unleaded Gasoline Exhaust With and Without Treatment with Iodine Vapor 80

XIII. Total Lead Body Burden in Deer Mice 91

XIV. Soil Leaching Studies 105

XV. System of Equations 118

XVI. Estimates of the Effect to the Industrial Organic Chemicals Industry from the Elimination of Lead from Gasoline 133

XVII. Employment Losses by Census Regions, Lead Smelting Industry 134

XVIII. Precision of the Method 146

XIX. Sources of Variation in Soil Analysis 146

XX. Comparison of Emission Spectrography vs. Atomic Absorption Analysis of Pb in Soil 151

XXI. Distribution of Pb as a Function of Particle Size on Sample #40-13 152

XXII. Recovery of Pb from a Soil Sample by AAS and ES 152

XXIII. Solvent Extraction of Lead from Soil 153

XXIV. Pb Content of 8x10-Inch Glass-Fiber Filters 154

XXV. Comparison of Dry Ashing vs. Wet Digestion on Glass-Fiber Filter Samples 155

XXVI. Lead Content of Filters on Storage, $\mu g/in^2$ 158

XXVII. Comparative Pb Analysis of Organs by AAS and Colorimetry 160

LIST OF FIGURES

1. Impact on Man of Environmental Contamination Caused by Lead: Chronology 19
2. Model for Flow of Traffic Exhaust Through Environment 40
3. Four Bivane Anemometers Deployed for Field Test 43
4. Sensing Unit, Bivane Anemometer 43
5. Anemometer Affixed to Portable Mast 44
6. Truck Trailer Transport System 47
7. Winch in Operation 47
8. Fully Extended Mast 48
9. Recorder Unit 49
10. Recorder and Display Consoles in Camper Truck 53
11. Pickup Truck with Camper 54
12. Hoist and Generator 54
13. Propane-Powered Generator 55
14. Trailer with Masts 55
15. Traffic Volume Map of Denver-Fort Collins Area 59
16. Topographic Map, 144th Avenue Overpass Sampling Site 60
17. Topographic Map, Timnath Exit Sampling Site 61
18. X-Ray Spectra of PbClBr 67
19. Volumetric Apparatus for Measuring Adsorption of Hydrocarbon Vapor on PbBrCl 69
20. The Solubilities of $PbCl_2$, $PbBr_2$, and PbClBr in Water as a Function of Temperature 71
21. Electrostatic Collector 75
22. Exhaust Collection Apparatus, Disassembled 76
23. Exhaust Collection Apparatus, Assembled in Exhaust Stream 76
24. CSU Isothermal Cloud Chamber 79
25. Ice Nucleating Characteristics of Exhaust 81
26. Average Annual Concentration of Ice Nuclei Active at -20°C 83
27. Average Activation Spectrum for Ice Nuclei 85
28. Ice Nuclei Activation Spectra for Auto Exhaust from Two Cars 86
29. Lead Accumulation in Soil Adjacent to Roadway 96
30. Lead Accumulation in Soil Adjacent to Roadway at One Inch Intervals 98

31. Depletion of ^{210}Pb from Solution by Soil 100
32. Uptake of Lead from Solution by Soil 102
33. Uptake of Lead from Solution by Soil 103
34. Adsorption of Lead from Solution on Soil at 30°C 104
35. Uptake of Lead from $Pb(NO_3)_2$-Doped Soil by Plant Shoots 108
36. Flow Diagram for Environmental Transport of Lead from Traffic Exhaust 111
37. Generalized Flow Chart for Production of Lead-bearing Antiknock Gasoline Additives 123
38. Flow of Goods and Services Among Sectors Concerned with Lead 130
39. Flow Chart for Emission Spectrographic Method for Lead in Soil 144
40. Calibration Curves for Determination of Lead by Emission Spectrography 145
41. Scattering and Molecular Absorption from Digested Blood Sample 149
42. Effects of Time and HNO_3 Concentration on AAS Lead Determination 156
43. Effect of HNO_3 Concentration on AAS Lead Determination 157

1. SUMMARY

General. An interdependent, interdisciplinary research team at Colorado State University is studying the broad aspects of environmental contamination caused by lead. Eight professors from six academic departments in three colleges at CSU are the faculty investigators. The objectives of the research are (1) to develop and test an interdisciplinary approach to the study of environmental pollution problems using lead as an example, and (2) to evaluate consequences of lead pollution from traffic exhaust and economic and technological effects of steps taken to reduce lead pollution from this source. Emphasis during the phase of the program covered in this report is upon pilot experiments to determine where, in what forms, and at what rate lead from traffic exhaust is accumulating in the environment. Additional research deals with the potential of traffic exhaust for inadvertent weather modification and social and economic consequences of steps taken to shut off the flow of lead to the petroleum industry. The focal point for experiments described herein is measurement of lead transport from Interstate Highway 25 at selected sampling sites in Colorado. Experiments to characterize lead uptake by site soils and biota are also discussed.

Atmospheric Transport. Instrumental capabilities for measuring atmospheric lead transport have been designed, constructed, and tested. Instrumentation has been tested under field conditions, and pilot experiments have been completed. Continuing work is concerned with measurement of meteorological factors affecting dispersion of automotive lead from Interstate Highway 25.

Cloud Chamber Tests. Ice crystal production per liter of exhaust is essentially identical for leaded and lead-free fuel at -22°C for the samples tested. While the number of ice crystals produced after iodination is 100 to 1000 times greater than that for untreated exhaust, again there is little difference between leaded and lead-free gasoline. If lead containing particulate matter from automobile exhaust can act as an ice nucleant, or if lead iodide produced upon exposure of exhaust to iodine vapor can act as an ice nucleant, it must be concluded that the effect of lead is minor compared to the nucleating abilities of other exhaust components, both in the presence and absence of iodine. It therefore seems unlikely from studies thus far carried out that switching to lead-free gasoline would appreciably reduce the potential of traffic exhaust for inadvertent weather modification. Continuing work is concerned with identification of exhaust constituents other than lead which can be activated for ice nucleation.

Possible Inadvertent Cloud Seeding. Cloud chamber tests show that while unaltered automobile exhaust can produce large numbers of ice nuclei at cooler temperatures, nucleation activity of automobile exhaust is indistinguishable from background at temperatures warmer than about -18°C. This is the temperature region for which an increase in precipitation from inadvertent seeding should occur. Since natural nuclei occur in sufficient numbers at temperatures of about -24°C and colder, the net effect of an increase in ice nuclei at these colder temperatures would be overseeding which could result in a precipitation decrease. Continuing work deals with effects of nucleation temperature, aging, and exposure to various atmospheric constituents.

Accumulation of Lead in Animals. Mice collected along Interstate Highway 25 in Colorado show a total body burden of lead approximately three times higher than that for mice collected from a remote mountainous region in Colorado. While the major pathway may be ingestion of lead-contaminated food and water, inhalation of lead-containing air may also be an important pathway. An organ-by-organ lead analysis is underway. Arrangements have been made to obtain tissue samples from Larimer County coroner cases in the State of Colorado. Effects of subclinical exposure to TEL upon animal behavior are under investigation.

Lead in Soil. Lead from traffic exhaust is rapidly immobilized in upper soil strata. The capacity of soil for lead immobilization is quite high. Solubility tests indicate that approximately 1% of lead found in highly contaminated soil can be classified as lipid-soluble. For the soil-plant combinations investigated thus far, plants absorb very little lead from soil. Continuing experiments deal with translocation of lead in plants and effects of soil composition on lead uptake.

Economic Aspects. An input-output economic analysis of industrial sectors involved in production of tetraalkyl lead antiknock compounds reveals that if the flow of lead to the U.S. petroleum industry were shut off, approximately 11,900 jobs would be eliminated. Specific regional effects, with which the continuing study deals, could be quite severe in certain areas. Work in progress is concerned with use of economic data for decision making in pollution problems of which lead is one example.

Chemical Analysis. A central service for chemical analysis of lead project samples has been established. The primary analytical techniques are atomic absorption spectrometry and emission spectroscopy by which samples are routinely analyzed for lead at the microgram level. Additional capabilities are based on a microwave excitation technique and the AAS sampling boat technique which allow determination of lead at the nanogram level. Work in progress deals with improvement of analytical service and identification of lead species present in various environmental media.

Transport Model. A conceptual model has been developed for movement of automotive lead through the environment. The model provides an integrated picture of the transport problem and its components and is helpful in planning and coordinating various research tasks. Some progress has been made toward analytical formulation, and work underway is concerned with mathematical development needed for quantitation.

User Groups. User groups are of two types: those concerned with lead additive manufacture, distribution, consumption, and regulation; those concerned with evaluation methodologies for pollution problems, particularly those with a significant atmospheric component. Individual project scientists have established ties with user groups in both categories. Strong ties have been established with certain state and federal decision makers. Special efforts are underway to strengthen ties with additional user groups, especially those concerned with standard setting and enforcement.

Interdisciplinary Team Approach. Problem-focused interdisciplinary research can be carried out successfully in an academic milieu provided that lines of communication among participants can be established and maintained. All major scientific decisions involve group participation, and collaboration among participants on specific research tasks occurs at the working level. Considerable time during the first year was devoted to technique development and refinement: participants have willingly undertaken such service-function activities as an expression of the cooperative nature of this investigation. It is hoped to further strengthen communications between the CSU team and research teams concerned with trace metals pollution at other institutions.

I. BACKGROUND

Few pollution issues have commanded more attention and aroused more controversy than the question of continued use of lead antiknock compounds in gasoline. There is disagreement concerning consequences of lead pollution from traffic exhaust, and there is disagreement concerning technological and societal consequences for measures proposed to reduce the lead content of gasoline.

Table I shows industrial lead consumption in the United States during the period 1966-1969 (Lutz _et al_., 1970). The annual combustion of lead in gasoline amounts to approximately 5 x 10^8 pounds in the United States and 7 x 10^8 pounds on a global basis. While use of lead for gasoline is second to that for storage batteries, no other single source of lead would pose a comparable potential for pervasive environmental transport. The fraction of combusted lead available for long-range atmospheric transport is not known with certainty, but current estimates are that over the life of a vehicle about 70% of combusted lead becomes airborne (Habibi, 1970) with the remainder retained by the vehicle. Gravitational settling rapidly removes large lead-bearing particles very near the roadway.

Arguments against continued use of lead in gasoline are outlined in Table II. Perhaps the most persuasive technological argument is that lead can interfere with the operation of catalytic pollution control devices. Such devices have been developed or are under development for converting carbon monoxide to CO_2 and oxidizing unburned hydrocarbons. Additionally, some devices show promise for reducing oxides of nitrogen.

TABLE I

INDUSTRIAL LEAD CONSUMPTION IN THE UNITED STATES

(In Short Tons)

	1966	1967	1968	1969
Storage Batteries	472,492	466,665	513,703	558,121
Oil Refining & Gasoline	246,879	247,170	261,897	271,128
Pigments	119,888	103,190	109,734	101,866
Solder	78,898	68,883	74,074	65,126
Ammunition	78,435	78,766	82,193	77,805
Cable	66,491	63,037	53,456	54,078
Construction (caulking)	63,250	48,789	49,718	41,888
Printing (type metal)	30,421	28,554	27,981	26,469
Total classified	1,156,754	1,105,004	1,172,756	1,196,501
Unclassified	167,123	155,512	156,034	178,699
Grand total	1,323,877	1,260,516	1,328,790	1,375,200

Lutz *et al*., "Lead Model Case Study," Battelle Memorial Institute Research Report (1970).

While there is some evidence that catalytic treatment of automobile exhaust may promote generation of ammonia (Hunter, 1971), the catalytic approach for automotive emission control is favored for meeting the 1975 EPA standards (J. APCA, 21, 352 (1971)).

Since lead is toxic, it is argued that as little as possible should enter the environment as a by-product of the activities of man (Craig *et al*., 1971). People living or working in areas nearby heavily traveled highways can have higher blood lead levels (Goldsmith, 1969). Autopsy data indicate that citizens of highly industrialized countries in which use of lead antiknock compounds is widespread accumulate lead in bone and aorta (Schroeder, 1968). While lead from traffic exhaust may be a factor in the high incidences of pediatric plumbism reported for several major cities (Chisolm, 1971), present thinking is that ingestion of lead from putty and paint and lead leached from pottery are the major sources. It is now well known that cases of pediatric lead poisoning in large cities increase appreciably during the summer months (Chisolm, 1971; Guinee, 1971). While the explanation may be increased exposure to sunlight which may mobilize previously deposited lead, the victims may also be ingesting larger quantities of deposited lead fallout coating objects which children place in their mouths. Cases of lead intoxication in zoo animals have been attributed to atmospheric lead pollution (Bazell, 1971).

TABLE II

ARGUMENTS AGAINST LEAD IN GASOLINE
Catalytic pollution control devices
Human health hazard
Inadvertent weather modification
Maintenance costs
Possible ecological disruptions

Schaefer (1968, 1969) and Morgan (1968) have suggested that traffic exhaust containing lead may pose a significant potential for inadvertent weather modification. Lead iodide is second only to silver iodide as an effective ice nucleant. Threshold temperatures for silver iodide and lead iodide are -4°C and -6°C, respectively (Mason, 1962). Atmospheric iodine levels in seacoast areas reach five nanograms, per cubic meter (Lininger et al., 1966). Thus iodination of atmospheric lead cannot be ruled out on a concentration basis. Other particulates from traffic exhaust have also been considered in terms of weather modification effects (SCEP group, 1970).

Automobile maintenance costs may be lower if lead were removed from gasoline (Allen, 1970). Lead-containing deposits can accumulate and reduce combustion efficiency. Most lead is scavenged from the engine by ethylene dibromide and ethylene dichloride which promote formation of volatile lead halides. However, corrosive hydrohalic acids are unwanted by-products of the scavenging process.

There is concern for possible subtle ecological disruptions caused by heavy metals in the environment (SCEP group, 1970). While such low-level effects have thus far not been detected for lead, it can be argued that effects may not be manifested for several generations yet to come, and reduction of lead use would represent a positive step to protect the environment. Measurements of lead in Greenland snow as a function of depth indicate that lead levels have been increasing steadily since the use of lead additives in gasoline became widespread. Determination of the isotopic composition of the lead found might settle the question of whether the accumulated lead was deposited through long-range atmospheric transport of lead particles originating in traffic exhaust (Murozumi et al., 1969). While earlier studies indicate no discernible increase in urban atmospheric lead levels (Dept. of Health, Education, and Welfare, 1965), later work indicates that the atmospheric lead levels in San Diego are increasing with time (Chow, 1970). More data are being accumulated to determine whether the trend is statistically significant with respect to variability in sampling and analysis.

Arguments for continued use of leaded gasoline are outlined in Table III. Estimates on the conversion to unleaded and low-lead gasolines seem to agree that the new gasolines will cost more (C&E News, November 9, 1970). The cost of adding lead to gasoline is approximately 0.6-0.7¢ per gallon; industry estimates for consumer cost increases for unleaded gasolines range from approximately 2¢ per gallon to about 6¢ per gallon which could require billions of dollars for modifying refinery equipment. Other antiknock compounds have been considered to replace tetraethyl lead in gasoline. While some nonmetallic organic compounds do possess antiknock properties, they are far less effective than organometallics (Env. Sci. & Tech., June, 1971). While one compound, methyl cyclopentadienyl manganese tricarbonyl, does show promise, the environmental consequences of switching to other organometallics have not received adequate study.

TABLE III

ARGUMENTS FOR LEAD IN GASOLINE

Unleaded gasolines more expensive
No known adverse health effects
Unleaded gasolines may increase smog-forming emissions
Unleaded gasolines may increase carcinogenic emissions
Particulate traps can remove lead
Lead prevents exhaust valve damage

Those favoring continued use of lead in gasoline point out that there are no known adverse health effects attributable to the present atmospheric lead levels from traffic exhaust. Early work indicated that lead from traffic exhaust may be a significant factor in visibility reduction in urban areas (Charlson, 1969); more recent work (Pierrard, 1971) indicates that the visibility reduction attributable to combustion of unleaded gasoline would be considerably greater than that for leaded gasoline. Combustion of unleaded gasoline may produce more smog-forming emissions than combustion of leaded gasolines, a series of Bureau of Mines tests suggests (Eccleston, 1970). Those smog chamber tests indicate that gasoline compositions typical of those envisioned for unleaded gasolines do produce larger quantities of photochemically reactive hydrocarbons under certain test conditions. There is also some evidence that unleaded gasolines high in aromatics may increase production of carcinogenic polynuclear hydrocarbons, namely benzo(a)pyrene and dibenzanthracene (Jacobs, 1971; Begeman, 1970). E. I. du Pont and Ethyl scientists claim that lead can be effectively removed from vehicular exhaust by means of particulate traps (Cantwell, 1970; Habibi _et al_., 1970; Hirschler _et al_., 1970).

Reports concerning the fraction of lead combusted available for long-range atmospheric transport disagree. Hirschler's work (1957) would suggest that very little of the lead combusted is of sufficiently small size to travel very far from a roadway. Measurements of a mass median equivalent particle size diameter of about 0.25 μ are reported by Robinson (1963) and Mueller (1963). These measurements have been interpreted incorrectly by some workers who conclude that virtually all of the lead combusted is sufficiently small to have negligible settling velocity. Rather elaborate test facilities were developed somewhat later (Habibi, 1970; Habibi et al., 1970). The test procedure allowed a more accurate materials balance to be constructed for the amount of lead consumed. These tests indicate that the fraction of lead injected into the atmosphere is highly dependent upon operating conditions and accumulated vehicle mileage.

A final point in favor of keeping lead in gasoline deals with reported cases of exhaust valve damage with prolonged use of unleaded gasolines under severe conditions (Hyman, 1971; Felt et al., 1970). Presence of lead in gasoline apparently leads to formation of a lubricating film between the exhaust valve and seat, without which exhaust valve life is drastically shortened (C&E News, November 9, 1970). Other additives have been studied, particularly phosphorus-containing compounds, to accomplish the same end, but environmentalists have raised objections to further massive dissipations of phosphorus (Taliaferro, 1970).

Even though many of the technological, environmental, and societal questions concerning continued use of lead in gasoline are not yet answered, public pressure to ban the use of lead in gasoline is apparently having its effect on the production of lead alkyls. According to a recent U.S. Bureau of Mines survey, consumption of lead alkyl antiknock compounds was down 16% in the first four months of 1971 compared to the consumption for the same period in 1970 (C&E News, July 12, 1971). Japanese plans to build an additional TEL facility were scrapped (C&E News, January 18, 1971), and Mitsubishi Chemical Industries will supply isobutene dimer to replace isooctane in gasoline blending. The advantage would be that only about 1/10 as much tetraethyl lead is needed for the same gain in octane rating (C&E News, June 14, 1971). Whatever the final disposition of the lead issue, it seems clear from industrial response thus far that the demand for low-lead and lead-free gasolines will increase. Whether the removal of lead from gasoline is accomplished by persuasion or by means of legislation or some combination thereof, many environmentalists both in and out of government feel that this action is essential if the 1975 EPA air quality standards are to be achieved. The Environmental Protection Agency has not yet established air quality standards, either ambient or emissions, for lead; however, the matter is receiving considerable study.

Regardless of the ultimate outcome of efforts to curtail and ultimately ban the use of lead in gasoline, it is of great national importance that a mechanism be developed for assessing environmental pollution problems, of which lead is but one example. If an assessment capability can be developed for lead, this capability can be extended to other substances such as combustion-produced carcinogens, other combustion released metals. and other fuel additives such as nickel and boron. Even though use of lead in gasoline may decrease over the next few years, there will remain rather enormous quantities of lead in the environment which originated in the combustion of leaded fuels. Since lead in the environment is apparently immutable, the environmental lead problem (if such a problem exists) may not go away when leaded fuels are removed from the market. The time required for the atmosphere to cleanse itself after curtailment of combustion of leaded fuels is also of considerable scientific interest. While lead sales have decreased, no corresponding decrease in atmospheric lead levels has yet been detected. The lead issue thus offers many possibilities for determining the history of a trace metal in the environment.

A combination of a number of societal, environmental, and technological factors makes the lead issue particularly appropriate for scientific study. The lead issue touches the lives of most Americans, either directly or indirectly. The amounts of lead entering the environment as a result of man's activities are larger than those for most trace metals with possible harmful effects for man. The societal consequences for lead pollution are thus potentially much greater than for other trace metals. The economic consequences of switching to low-lead and lead-free gasoline are considerable, and cost increases as well as possible savings will be passed along to virtually all Americans. In summary, the magnitude of the lead issue distinguishes it from most other trace metal pollution problems.

In terms of physical and chemical considerations, the lead issue is also distinguishable from other trace metal pollution issues. Lead is ubiquitous in the earth's crust with an average concentration of about 16 ppm. When compared to the amounts of lead entering the atmosphere as a result of man's activities, very little atmospheric lead can be traced to natural environmental processes. The major source of lead in the upper atmosphere is radioactive decay of radon, and in the lower atmosphere some suspended lead may be traced to injection of lead-containing soil. While methods of chemical analysis for detecting and measuring lead are quite satisfactory at the ppm level and reasonably good at the ppb level, natural background lead levels are high compared to those for other trace constituents such as selenium, arsenic, and pesticide residues from agricultural activity. The variability in natural background lead levels is generally quite high. While it may be possible to identify the source of lead contamination in a given environmental sample by a lead isotope-ratio technique (Ault, 1970), variability in the isotopic ratios is also quite high and may limit the general utility of the technique (Nathans, 1971). Thus, developing an assessment capability for problems attributable to trace metals in the environment based on the example of lead may have considerably more general validity than an assessment capability developed on using another trace constituent as the example. Many factors must be considered in the lead issue which may also require consideration for other trace substances regarded as environmental contaminants. Thus the study of lead may serve as a model for the study of other environmental trace constituents.

OBJECTIVES AND APPROACH

A. Introduction

The NSF-sponsored study of environmental lead began at Colorado State University on July 1, 1970. Eight faculty investigators from six departments in three colleges are collaborating in the study. The ultimate objectives are to develop an interdisciplinary approach to the study of environmental pollution problems using lead as an example, and to evaluate consequences for environmental contamination caused by lead from traffic exhaust including technological and societal consequences of measures to reduce lead pollution.

B. Objectives

Research objectives originally proposed for the three-year study are listed below in outline form:

First Year:
1. Characterize the compounds of lead entering the atmosphere.
2. Determine the logistics and scale for the field studies.
3. Obtain gross cause and effect relationships for soil retention of lead under laboratory conditions.
4. Determine whether lead-bearing exhaust offers a significant potential for inadvertent weather modification.
5. Obtain structural model for lead and related industries.

Second Year:

1. Characterize compounds of lead in atmospheric fallout.
2. Determine from field study the rate and range of lead transport from the line source.
3. Characterize transport and retention in soil under field conditions.
4. Determine 12-month bioaccumulation cycle for species near line source.
5. Identify atmospheric constituents which activate lead for ice nucleation.
6. Identify distinctly social regional effects associated with lead.

Third Year:

1. Evaluate diffusion and washout mechanisms for atmospheric transport.
2. Map out hazardous city-corridor accumulation conditions.
3. Determine effects of other atmospheric constituents on activation of lead for ice nucleation.
4. Determine effects of plants on transport and retention in soil; determine standards by means of overload experiments.
5. Determine rates and routes for bioaccumulation of lead; determine standards by means of overload experiments.
6. Evaluate costs and benefits associated with specific socioeconomic alternatives.

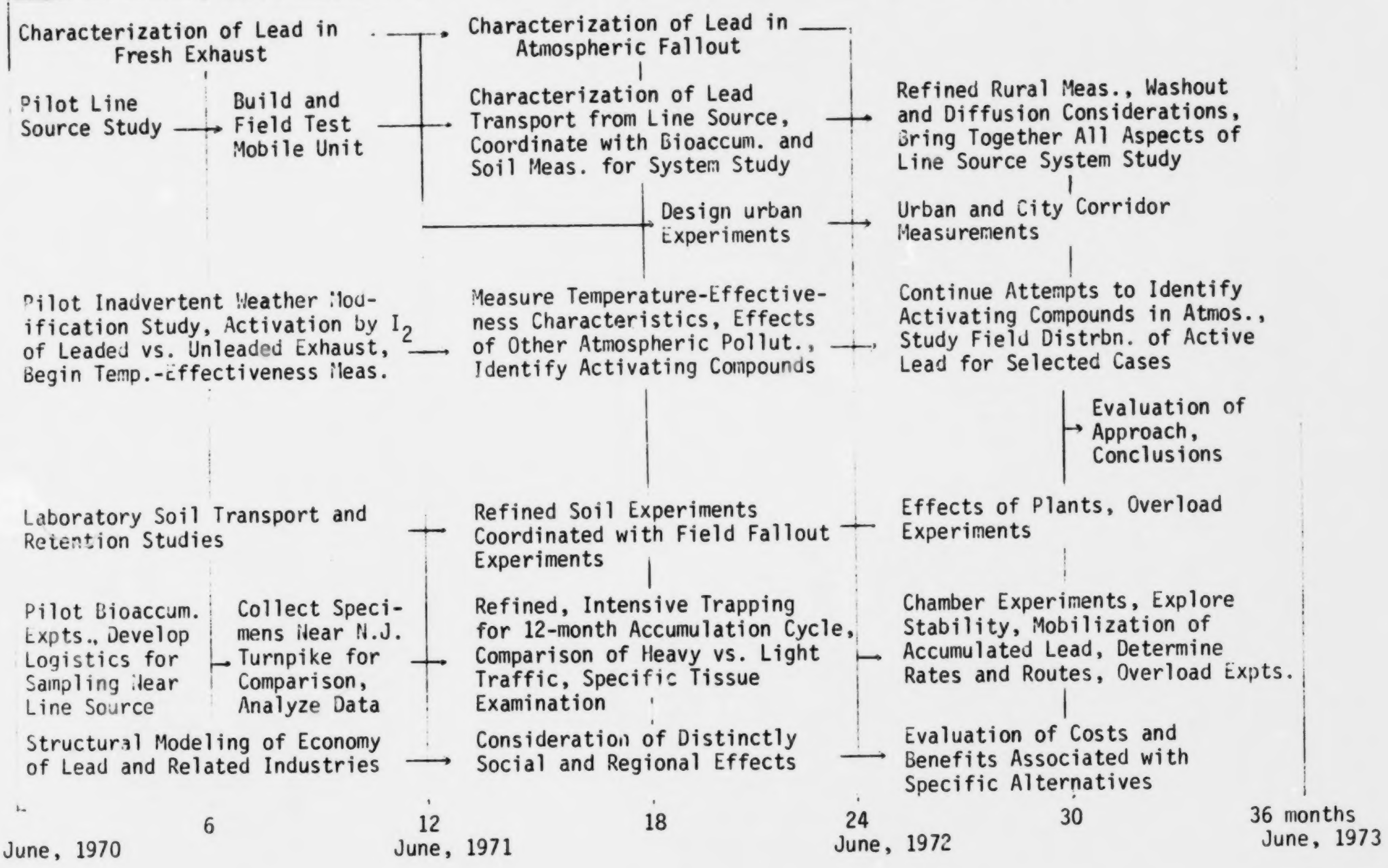
7. Evaluate systems approach for applicability to other environmental contaminants.
8. Formulate conclusions.

A chronology of the research tasks is depicted in schematic form in Figure 1. Lines connecting activities are intended to show the flow of information among interdependent research tasks. First year activities proceeded along the lines outlined originally with few exceptions. Exceptions were occasionally necessitated by need for development of experimental techniques, particularly in the area of air sampling and chemical analysis. While the need for such technique development has slowed progress in a few areas, much of the technique development has been accomplished, and research has resumed in these areas.

Other research tasks have been accomplished more quickly than was anticipated initially. For example, intensive trapping experiments were initiated during the first year, well ahead of schedule. Field soil data have already been obtained, but the laboratory soil transport and retention studies are continuing. The desirability for specimen collection near the New Jersey turnpike is under study because bioaccumulation studies have appeared in the literature since initiation of the project; moreover, results of our own trapping experiments indicate a significant difference in the level of lead accumulation between mice trapped near I-25 and mice collected from a remote region of Colorado Instrumental capabilities for measuring atmospheric transport were completed approximately on schedule, and field measurements are underway. Atmospheric chemistry of lead poses special difficulties in view of need for development of new experimental techniques.

Figure 1

IMPACT ON MAN OF ENVIRONMENTAL CONTAMINATION CAUSED BY LEAD: CHRONOLOGY


Characterization of Lead in Fresh Exhaust
Characterization of Lead in Atmospheric Fallout
Pilot Line Source Study
Build and Field Test Mobile Unit
Characterization of Lead Transport from Line Source, Coordinate with Bioaccum. and Soil Meas. for System Study
Refined Rural Meas., Washout and Diffusion Considerations, Bring Together All Aspects of Line Source System Study
Design urban Experiments
Urban and City Corridor Measurements
Pilot Inadvertent Weather Modification Study, Activation by I2 of Leaded vs. Unleaded Exhaust, Begin Temp.-Effectiveness Meas.
Measure Temperature-Effectiveness Characteristics, Effects of Other Atmospheric Pollut., Identify Activating Compounds
Continue Attempts to Identify Activating Compounds in Atmos., Study Field Distrbn. of Active Lead for Selected Cases
Evaluation of Approach, Conclusions
Laboratory Soil Transport and Retention Studies
Refined Soil Experiments Coordinated with Field Fallout Experiments
Effects of Plants, Overload Experiments
Pilot Bioaccum. Expts., Develop Logistics for Sampling Near Line Source
Collect Specimens Near N.J. Turnpike for Comparison, Analyze Data
Refined, Intensive Trapping for 12-month Accumulation Cycle, Comparison of Heavy vs. Light Traffic, Specific Tissue Examination
Chamber Experiments, Explore Stability, Mobilization of Accumulated Lead, Determine Rates and Routes, Overload Expts.
Structural Modeling of Economy of Lead and Related Industries
Consideration of Distinctly Social and Regional Effects
Evaluation of Costs and Benefits Associated with Specific Alternatives
June, 1970
6
12
June, 1971
18
24
June, 1972
30
36 months
June, 1973

An additional study undertaken which was not specified in the original work plan is a limited attempt to construct a conceptual and analytical model for short-range environmental transport of automotive lead. It is hoped to realize sufficient analytical formulation in the next twelve months to permit some quantitation. The model has proved to be an important and useful addition to the work scope of the program. An attempt to develop a comprehensive ecosystem model for the movement of lead through the environment is under study by the University of Illinois group. However, that model does not deal specifically with short-range transport of automotive lead from a highway. An additional research task of limited scope was undertaken to investigate the interaction of microbial systems with automotive lead.

C. Interdisciplinary Approach

An interdependent, interdisciplinary research team was formed to carry out the research. Participants are identified in Table I. Disciplines included are physical chemistry, meteorology, atmospheric chemistry, resource economics, agricultural chemistry and soil, cloud physics, analytical chemistry, and environmental physiology. The diverse backgrounds of the investigators are brought together for application to the broad problem of environmental contamination caused by lead. In the discussions that preceded preparation of the proposal, the broad problem was approached in terms of fundamental questions which need to be answered for an assessment of the environmental impact of lead from traffic exhaust. Some of the questions can be answered by means of research in a very narrow field; other questions require the

TABLE IV

COLORADO STATE UNIVERSITY ENVIRONMENTAL LEAD PROJECT

RESEARCH PARTICIPANTS

Faculty Investigators

*H. W. Edwards, Associate Professor of Mechanical Engineering
M. L. Corrin, Professor of Atmospheric Science
L. O. Grant, Professor of Atmospheric Science
L. M. Hartman, Professor of Economics
E. R. Reiter, Professor of Atmospheric Science
R. K. Skogerboe, Associate Professor of Chemistry
C. G. Wilber, Professor of Zoology
R. L. Zimdahl, Assistant Professor of Botany and Plant Pathology

Research Associate

T. G. Tornabene, Assistant Professor of Microbiology (Summer, 1971)

Graduate Research Assistants

Jon Arvik, Botany and Plant Pathology
Alex Bejmuk, Chemistry
Paul Katen, Atmospheric Science
Ronald Rinehart, Atmospheric Science
Elias Saig, Economics
Richard Springborn, Atmospheric Science
Donald Vaitkus, Mechanical Engineering
William Welch, Zoology

Senior Research Technicians

Gary Cobb, Atmospheric Science
Donald Dick, Chemistry

Summer Students

Gary A. Dick
Thomas M. Mischke
Gerald R. Schultz
Martha A. Shea

*Principal Investigator and Program Coordinator attention of researchers from several disciplines. Thus evolution of the research program has been from a statement of the overall problem to the delineation of specific questions to the naming of the required disciplines. It is emphasized that the team-effort approach arose naturally from the broad nature of the problem.

An academic community offers a distinct advantage for problem focused research. Not all university researchers will be attracted to such projects. For many professors and students, problem focused research may not represent the appropriate avenue for their intellectual contributions. For others, especially those who are sensitive to public need, problem focused research represents a mechanism for involvement in an activity with societal relevance. Furthermore, many scientists welcome opportunities to broaden their perspective of their own field and seek exposure to other viewpoints. Our experience in this regard is that students and faculty are quite frank in expressing their inclinations toward problem focused research. The result is that the ultimate composition of the research team not only reflects competences from diverse fields, but, and perhaps equally important, consists of participants who are enthusiastic and share a common problem solving objective.

We found that a fair amount of the first year's effort was devoted to technique development and adaptation. Development of measuring capabilities and experimental procedures involves application of existing knowledge to the specific problems at hand. For example, it has been found necessary to adapt the usual APCO procedure for measuring atmospheric lead to the specific short-term sampling needs of this project. Another example is the measurement of low lead levels in environmental samples containing relatively large amounts of particulate matter and silica. These efforts should be regarded as developmental research to provide capabilities basic to specific project requirements. It is essential that participants share a willingness to participate in such technique development.

Because the project is being conducted in an academic milieu, training students to function effectively in an interdisciplinary environment is an important goal. While students retain a clear departmental identity, the interdisciplinary nature of their research involvement distinguishes them from their departmental colleagues. We have not attempted to produce generalists per se; rather, these students are specialists in established disciplines who have elected to bring their talents to bear on the solution of a particular aspect of a common problem. The enthusiasm and dedication of these students are refreshing and most welcome. A student's graduate program is developed on an individual basis by the student's graduate committee which is typically interdisciplinary in composition. The program can thus be tailored to the specific academic and professional aspirations of the student.

All major scientific decisions involve group participation. If a change in emphasis is indicated, input is obtained from each of the faculty investigators. An interdisciplinary project should not be an externally directed project. Major scientific decisions should be made with participation at the working level.

A final point deals with safeguards against fragmentation of the project into a number of autonomous research tasks. It might be possible for those engaged in interdisciplinary research to become overly absorbed in their own segment of the project, and consequently develop the desire to take what they regard as their portion of project resources and go their own way until the final report time comes around. The only interdisciplinary feature of such a program would be the staple that holds together the segments contributed to the final report. Such an arrangement defeats the spirit and intent of problem focused interdisciplinary research. It is therefore desirable to establish a mechanism by which the occasional wayward investigator can be encouraged to renew his group identity.

Universities have been sharply criticized for sluggishness in mobilizing talent for problem focused education and research. In spite of a national shortage of broadly trained professionals to deal with environmental and societal problems, the 1969 report to the President's Environmental Quality Council concluded that few universities have developed meaningful interdisciplinary programs dealing specifically with solutions for major national problems. Lack of impressive success was attributed to intense competition for funds among established programs, need for faculty reward structure in problem focused programs which cut across traditional departmental lines, and need for substantial flexibility in introducing new curriculum requirements.

Cooperation across departmental and disciplinary lines might pose difficulties for academic institutions with especially rigid and orthodox structures, but our experiences are largely favorable. Problems that do arise, scientific or otherwise, are handled within the group at the working level. Factors which are favorable to the conduct of this project in that regard are internal control of staffing and fiscal considerations. An unfavorable factor is that it is difficult to bring all project participants together at the same time and location. While this has not been a major problem, an arrangement is currently being explored by which participants can spend a part of each week together in the same physical facility. We do not know whether this will enhance our research capability, but it is an experiment which needs to be conducted.

D. Group Meetings

Regular group meetings of the entire research team are held at approximately bimonthly intervals. The meetings serve two important purposes. Group meetings have encouraged faculty investigators and graduate students to consider broader aspects of their individual research activities. Group meetings have been helpful in focusing attention on specific topics of current interest. Both general sessions and seminars devoted to specific topics have been held. General sessions are useful for reviewing progress and revealing areas requiring increased emphasis. We have found that collaboration among participants occurs at the working level largely as a result of commonality of objectives and regular meetings of the entire research team. During the first phase of the program, provision was made for a number of invited lectures by experts in various fields. However, the latter sessions did not adequately stimulate communications among participants, and meaningful collaboration among investigators on laboratory projects developed naturally when the flow of information among participants became an accomplished fact. The group meetings have thus evolved into collaborative working sessions where research progress on a particular segment of the program is reviewed, the significance of the result ascertained, and future experiments are planned.

Discussion leaders for technical sessions devoted to specific topics have been project faculty investigators, students, and visitors from other institutions. Notes are made and distributed for major meetings. Meetings involving the entire research team are listed below:

Date	Subject	Discussion Leader
August 6, 1970	Meteorology	E. R. Reiter Colorado State University
August 26, 1970	General	M. L. Corrin Colorado State University
September 17, 1970	Economics of Lead	L. M. Hartman Colorado State University
October 13, 1970	Lead Mining and Refining	R. Frush Colorado School of Mines
October 27, 1970	Inadvertent Weather Modification	L. O. Grant Colorado State University
November 10, 1970	General	H. W. Edwards Colorado State University
November 24, 1970	Analysis	R. K. Skogerboe Colorado State University
December 8, 1970	Goetz Aerosol Spectrometer	H. Gerber U.S. Army Electronics Command
January 13, 1971	Lead in the Environment	W. H. Allaway Cornell University
February 11, 1971	Aging of Lead Aerosols	D. A. Gillette NCAR
February 18, 1971	General	H. W. Edwards Colorado State University
March 11, 1971	University of Illinois Lead Project	B. B. Ewing, O. C. Braids University of Illinois
March 25, 1971	Public Policy Analysis	J. Gilmore University of Denver
April 7, 1971	Metabolic Aspects of Lead	C. G. Wilber Colorado State University
May 12, 1971	Meteorological Instrumentation	P. C. Katen, Graduate Student Colorado State University

May 25, 1971	Lead in Soil	R. L. Zimdahl Colorado State University
July 14, 1971	Automotive Lead: E. I. du Pont de Nemours & Co., Inc.	E. S. Jacobs L. A. Williams K. Habibi J. M. Pierrard R. C. Butler Wilmington, Delaware
September 28, 1971	Automotive Lead: Ethyl Corp.	G. L. Ter Haar W. E. Adams Ferndale, Michigan J. D. Fuller San Francisco, Calif. J. H. Laubach Denver, Colorado
October 9, 1971	Interaction of Lead with Microorganisms	T. G. Tornabene Colorado State University

Smaller meetings involving fewer project participants are held much more frequently. For example, matters involving characterization of environmental lead are typically discussed by H. W. Edwards, M. L. Corrin, R. K. Skogerboe, and R. L. Zimdahl. Transport of lead through the atmosphere is frequently discussed by M. L. Corrin, H. W. Edwards, E. R. Reiter, and R. K. Skogerboe. Petroleum refining equipment needs associated with massive conversion to unleaded gasoline might be discussed by H. W. Edwards, L. M. Hartman, M. L. Corrin, and C. G. Wilber. While the above project meetings have been successful in maintaining a high level of interest among project participants, it is emphasized that the meetings encourage participants with diverse backgrounds to collaborate in solving specific research problems. Participants seem comfortable with the present size of the group although some expansion in specific areas is needed. The present group size is sufficiently small to make the need for a tight internal administrative structure unnecessary. Some internal structure is applicable to the research tasks, however. Clearly identifiable groups of research tasks are the following: source characterization, transport, accumulation, and social and economic aspects.

E. Interaction with User Groups

Efforts have been made to identify and initiate communications with user groups for information generated by this project. User groups identified thus far are of two general types. The first consists of those concerned with manufacture, distribution, consumption, and regulation of lead antiknock gasoline additives. The second consists of those concerned with evaluation methodologies for trace contamination problems, particularly those that have a significant atmospheric component. National need is judged great for evaluation methodologies which will lead to rational societal action on environmental pollution issues. Lead is but one example of this type of trace contamination problem. Evaluation of environmental and technological consequences of massive combustion of lead-free gasoline represents a companion problem. The research team recognizes the need for communication of scientific findings during the course of the project as well as upon completion of the project. Publication in scientific journals by itself does not insure that the information will reach decision makers in time for planning and standard setting. In the sections that follow, specific interactions with user groups are described. Strong ties between individual project participants and certain federal and state decision makers have been established in key areas. More effort needs to be devoted to strengthening ties with regulatory agencies at the federal level.

1. Three-University Lead Study

The CSU study of lead from traffic exhaust is one element of a three-university attack upon the broad issue of lead in the environment.

An active partnership among the three participating institutions is developing. Information is exchanged on a regular basis, and CSU team members have traveled to the other two campuses on several occasions. H. W. Edwards and R. K. Skogerboe attended the University of Illinois Trace Metals Symposium in January, 1971. R. K. Skogerboe presented three papers dealing with analysis, sample treatment and handling, and evaluation of errors at this symposium. University of Illinois team members who visited the CSU campus during the first year are B. B. Ewing, O. C. Braids, and R. W. Woodhead. R. L. Zimdahl visited the Illinois soil group at Urbana in August, 1971, and H. W. Edwards visited the Urbana campus again in July, 1971. D. F. S. Natusch of the University of Illinois spent several months at the National Center for Atmospheric Research in Boulder and attended the July 14, 1971, CSU lead project seminar presented by visiting scientists from the E. I. du Pont Company. M. L. Corrin and R. K. Skogerboe attended the June, 1971, Conference on Trace Metals held at the University of Missouri during which some time was devoted to consultation with the University of Missouri team concerning atmospheric sampling and analytical methods. These exchanges of personnel contribute significantly to each team's broader understanding of the lead problem and components being studied on other campuses. Additional ties have been established with the Oak Ridge group through W. Fulkerson who visited the CSU campus during the summer of 1971. The Oak Ridge information retrieval service for information on trace metals has been utilized by the CSU team.

A program involving exchange of analytical samples among the three universities participating in the study of lead was initiated by R. K.

Skogerboe. Results from the University of Missouri team have been received; after receipt of the University of Illinois results and interpretation of the data, it is planned to issue a report of the findings. Common problems relating to analytical methodology, field sampling strategies, and need for standard samples have been identified. It is planned to continue coordination among the three analytical groups.

The three university programs are complementary, and the CSU team would welcome further strengthening of ties among the three campuses. It is anticipated that increasing emphasis for exchange of personnel will be placed upon collaboration in specific research areas. Initially, the primary objectives were to obtain a clear picture of the other institutions' programs, establish lines of communication, and identify areas of common interest. The CSU team competences are especially strong in the atmospheric sciences, and the program emphasizes the atmospheric component of lead pollution from traffic exhaust. The University of Illinois study emphasizes developing a total model for the transport of lead in a terrestrial ecosystem which contains a major aquatic component. The University of Illinois team has broad experience relevant to this ecosystem study with special strengths in ground water and sanitary engineering aspects. The University of Missouri study deals with environmental pollution from lead mining and smelting. The University of Missouri study is centered in the department of civil engineering on the Rolla campus; participation from the Columbia campus is included. The CSU team is also in communication with the University of Colorado group concerned with molybdenum pollution.

2. National

L. O. Grant is a member of the National Science Foundation Atmospheric Science Advisory Panel which evaluates the Foundation's research programs in this area. During the 1971-1972 fall quarter, L. O. Grant will spend approximately one month at the State University of New York at Albany. The major objective will be to collaborate with V. J. Schaefer concerning the role of pollution in inadvertent weather modification. C. G. Wilber serves as a consultant to several power-generating concerns who are planning to expand their activities using fossil-fuel-fired generating installations. In addition, he is also serving as a consultant to oil-shale developers and is trying to advise them on the best ways of preventing unacceptable impacts on the environment from their activities. H. W. Edwards serves as a consultant to the National Science Foundation to assist in evaluation of research proposals and participate in site visit inspections. H. W. Edwards is also conducting research in air pollution control sponsored by the Environmental Protection Agency. H. W. Edwards served as chairman for the American Chemical Society Symposium on Practical and Philosophical Aspects of Interdisciplinary Research, Bozeman, Montana, June 16-18, 1971. He presented a discussion of the CSU lead project and its relationship with the other two university lead projects at a meeting of the National Research Academy Subcommittee on Geochemical Environment in Health and Disease chaired by Helen Cannon in March, 1971. E. R. Reiter has developed strong ties with the Atomic Energy Commission and the National Aeronautics and Space Administration.

It is recognized that stronger ties with federal agencies, particularly those concerned with standard setting, are desirable. It is planned to intensify efforts to develop relationships by which the research team can effectively communicate its research findings to decision makers at this level.

3. Symposium on Interdisciplinary Research

Four members of the CSU team were invited to participate in the American Chemical Society Symposium on Practical and Philosophical Aspects of Interdisciplinary Research, Northwest Regional Meeting, held at Montana State University in June, 1971. CSU participants were H. W. Edwards (chairman), M. L. Corrin, R. K. Skogerboe, and R. L. Zimdahl. Papers were submitted by representatives from other institutions as well. Formal presentation of papers was followed by an informal question and answer session in which a number of "motherhood" and "apple pie" questions were addressed. The symposium was viewed by many to be a successful endeavor since as many as a third of the total attendees at the meeting were present for some of the papers. A descriptive account of the symposium with emphasis upon the CSU activities was published in Chemical and Engineering News.

4. Industry

Special efforts were made to obtain input from the industrial sector which is concerned with automotive lead. Teams from the E. I. du Pont de Nemours Co., Inc., and the Ethyl Corporation visited the CSU campus. Two-day group meetings were held on the occasion of each visit. An additional visitor from the industrial sector was D. R. Lynam, representing the International Lead Zinc Research Organization. The industrial scientists who traveled to the CSU campus were eager to make available their scientific knowledge to the CSU team. It is felt that such interactions are worthwhile, and since the lines of communication have been established it is expected that ties will be strengthened. Scientists from both the Ethyl Corporation and the du Pont Company indicated a desire to participate in exchange of standard samples. Implementation of such a round-robin analysis would be by R. K. Skogerboe.

5. State and Local

Strong ties have been established with certain state and local decision makers. M. L. Corrin is an alternate member of the Colorado Air Pollution Variance Board. He has also presented talks at environmental quality meetings in Denver, Boulder, and Littleton, Colorado and participated in the presentation of CSU environmental activities before the Colorado legislative committee. In Fort Collins, M. L. Corrin is a member of the Environmental Quality Committee for Designing Tomorrow Today, and he has presented numerous lectures and demonstrations before grade and high school classes on air pollution. He participated in Earth Day activities and spoke before various organizations on air pollution problems. Additionally, he testified before the Colorado Environmental Commission at its Fort Collins meeting.

L. O. Grant is a technical advisor to the Legislative Council, State of Colorado. Duties include providing technical input to the Council which is considering legislation on inadvertent weather modification.

Seminars concerning lead project activities have been given around the state at numerous meetings by M. L. Corrin, C. G. Wilber, and R. K. Skogerboe in the attempt to acquaint the public with the project. Press releases are given through the office of the principal investigator from time to time.

6. Colorado State University

Participating faculty members are all active within their individual departments in various programs of instruction and research. Most are involved in both graduate and undergraduate instruction. Most are involved in other research programs. All have been called upon from time to time to discuss the lead project in various classroom situations. H. W. Edwards participated in preparation of a manuscript for CSU Research, a widely distributed publication descriptive of CSU research and extension activities. He also worked with engineering students to develop a paper suitable for Slide Rule which is published during the academic year by CSU engineering students. Additionally, he is a member of the Environmental Engineering Committee which offers graduate and undergraduate seminar courses in environmental engineering.

M. L. Corrin is a member of the CSU Task Force on Environmental Programs and a member of the Environmental Studies Advisory Committee for implementation of an undergraduate environmental studies concentration. He is vice-chairman of the Environmental Resources Center Council, chairman of the Environmental Quality Committee for the Environmental Resources Center, and chairman of the Environmental Engineering Committee. M. L. Corrin has presented numerous lectures on air pollution for elementary courses in biology, chemistry, sanitary engineering and other disciplines.

7. Project Papers

The following is a list of project papers for the period covered by this report.

Corrin, M. L., "Lead in the Environment," presented at meeting of State legislators, cosponsored by Colorado State University and Colorado Bar Association, Denver, Colorado, February 24, 1971.

Corrin, M. L., "The Atmospheric Chemistry of Automotive Lead," presented at the 26th Northwest Regional Meeting, American Chemical Society, Bozeman, Montana, June 16-18, 1971.

Edwards, H. W., "Impact on Man of Environmental Contamination Caused by Lead," presented at meeting of National Research Academy Subcommittee on Geochemical Environment in Health and Disease, Denver, Colorado, March 30, 1971.

Edwards, H. W., "Air Pollution Control Devices," Environmental Engineering Lecture, Colorado State University, Fort Collins, Colorado, May 7, 1971.

Edwards, H. W., "Interdisciplinary Study of Lead Pollution," Mechanical Engineering Department Seminar, Colorado State University, Fort Collins, Colorado, May 27, 1971.

Edwards, H. W., "Interdisciplinary Study of Lead Pollution from Traffic Exhaust," presented at the 26th Northwest Regional Meeting, American Chemical Society, Bozeman, Montana, June 16-18, 1971.

Edwards, H. W., "Interdisciplinary Research Opportunities for Graduate Students," Mechanical Engineering Department Seminar, Colorado State University, Fort Collins, Colorado, October 5, 1971.

Edwards, H. W., "CSU Interdisciplinary Team Studies Environmental Lead," Slide Rule, 15(1), 2 (1971).

Grant, L. O., "On Air Pollutants as Ice Nuclei," presented at the 51st Annual Meeting, American Meteorological Society, San Francisco, California, January, 1971.

Skogerboe, R. K., "Environmental Research Directions at CSU," presented at the Fort Collins A.A.U.W. meeting, Colorado State University, Fort Collins, Colorado, November, 1970.

Skogerboe, R. K., "Analysis of Lead," presented at the Symposium on Heavy Metals, University of Illinois, Urbana, Illinois, January 7-8, 1971.

Skogerboe, R. K., "Sample Treatment and Handling," presented at the Symposium on Heavy Metals, University of Illinois, Urbana, Illinois, January 7-8, 1971.

Skogerboe, R. K. "Evaluation of Analysis Errors," presented at the Symposium on Heavy Metals, University of Illinois, Urbana, Illinois January 7-8, 1971.

Skogerboe, R. K., "Analytical Chemistry of Lead," presented at the 26th Northwest Regional Meeting, American Chemical Society, Bozeman, Montana, June 16-18, 1971.

Skogerboe, R. K. and W. A. Abbott, "Evaluation of Light Scattering and Molecular Absorption Interferences in Atomic Absorption Analysis of Biological Materials," presented at the 26th Northwest Regional Meeting, American Chemical Society, Bozeman, Montana, June 16-18, 1971.

Skogerboe, R. K., K. W. Olson, and T. R. Copeland, "Ultrasonic Versus Pneumatic Nebulization for Atomic Absorption - A Comparison," presented at the 26th Northwest Regional Meeting, American Chemical

Society, Bozeman, Montana, June 16-18, 1971.

Skogerboe, R. K. and W. Abbott, "Interferences in Atomic Absorption Analysis of Biological Materials," presented at the Rocky Mountain Spectroscopy Meeting, Denver, Colorado, August, 1971.

Skogerboe, R. K., "The Role of the Analytical Chemist in Environmental Research," Chemistry Colloquium, Colorado State University, Fort Collins, Colorado, September 29, 1971.

Skogerboe, R. K., J. Seeley, and D. Dick, "Sampling in the Environment," presented at the National SAS Meeting, St. Louis, Missouri, October, 1971.

Skogerboe, R. K., "Analytical Chemists - Who Needs Them!", to be presented at the Denver Spectroscopy Meeting (Local), Denver, Colorado, November, 1971.

Skogerboe, R. K., "Analytical Chemistry - Core Discipline of Environmental Research," to be presented at the Pittsburgh Conference on Analytical Chemistry, March, 1972.

Wilber, C. G., "Behavioral Aspects of Heavy Metal Toxicity," seminar presented at the United States Air Force Academy, September 29, 1971.

Wilber, C. G., "The Medico-Legal Aspects of Environmental Pollution," Trauma, in press.

Wilber, C. G., "Polluted Water - A Challenge to Forensic Biology," Journal of Forensic Sciences, 16(3), 251-268 (1971).

Zimdahl, R. L., "Soil Transport of Lead," presented at the 26th Northwest Regional Meeting, American Chemical Society, Bozeman, Montana, June 16-18, 1971.

Zimdahl, R. L., "Soil Fixation of Lead," presented at the American Society of Agronomy Annual Meeting, New York, New York, August, 1971.

IV. ATMOSPHERIC TRANSPORT OF LEAD

A. Introduction

One of the major sources of lead in the environment is vehicular exhaust. On a global basis the consumption of lead in gasoline is approximately 7 x 10^8 pounds per year, about half of which becomes airborne (Lutz et al., 1970). Consumption in the United States is approximately 5 x 10^8 pounds per year, with most of the remainder consumed in western Europe (Lutz et al., 1970). Measurements of lead concentrations in precipitation correlate well with gasoline consumption in the general area in which the measurements are taken (Lazrus et al., 1970). While there is still considerable disagreement concerning health effects attributable to present atmospheric lead levels (Konopinski and Upham, 1967; Blemel, 1967; Haley, 1969; Craig and Berlin, 1971), characterization of the environmental history of lead in its progress from sources to sinks and the impact upon the environment constitutes a challenging research task. The complex problem of lead in the environment is presently being attacked by a team effort with the attention focused upon lead from traffic exhaust. A rather complete understanding of atmospheric transport processes by which lead from traffic exhaust is dispersed is prerequisite to interpretation of measured lead uptake by soil, flora and fauna. Characterization of atmospheric transport of lead is heavily dependent upon and interactive with sampling and chemical analysis efforts as well as experiments to map out the lead accumulation patterns in soil.

The primary meteorological objective is to determine the range and extent of travel of lead from a major highway. Application of various line source diffusion equations to dispersion of lead from a heavily traveled highway account in the first approximation for observed (exponential) decreases in lead concentrations in both air and soil with distance from the highway (Lutz et al., 1970; Dedolph et al., 1970; Besner and Atkins, 1970; Motto et al., 1970; Daines et al., 1970; Schuck and Locke, 1970). The above models do not account for lead depletion due to gravitational settling, however. It has been reported that the lead to carbon monoxide ratio decreases with distance from the highway (Besner and Atkins, 1970; Atkins, 1969). While the measured lead accumulation patterns in Greenland glaciers (Murozumi et al., 1969) suggest that the major source is automotive exhaust, isotopic composition of these lead deposits does not yet provide conclusive evidence for long-range atmospheric transport of combusted lead. This possibility cannot be ruled out, however.

In view of past research and our own realization of the complexity of lead contamination in the environment from vehicular exhaust, we are attempting to develop a conceptual model for movement of lead from traffic exhaust through the environment. Input of atmospheric parameters into this model is indicated by dashed arrows in Figure 2. Certain effects such as cloud and precipitation processes, washoff from surfaces, reinjection into the atmosphere, and several others shown in Figure 2 are difficult to estimate with the present status of field measurement capabilities. The immediate efforts are therefore directed toward a simplified model dealing only with the heavily outlined boxes of Figure 2. This does not mean that the other boxes can be considered unimportant. For instance, reinjection into the atmosphere by strong winds

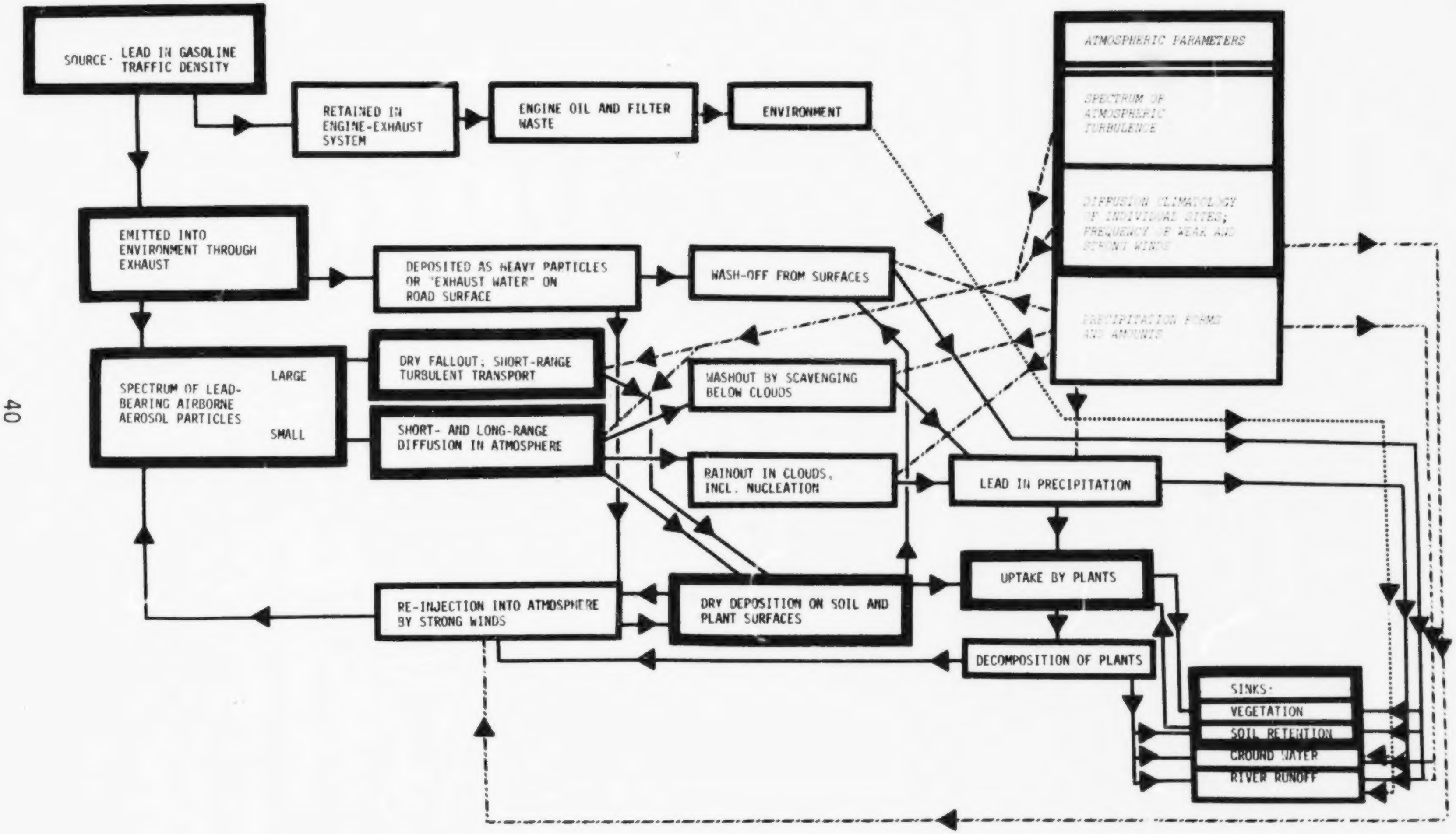

SOURCE: LEAD IN GASOLINE TRAFFIC DENSITY
RETAINED IN ENGINE-EXHAUST SYSTEM
ENGINE OIL AND FILTER WASTE
ENVIRONMENT
EMITTED INTO ENVIRONMENT THROUGH EXHAUST
DEPOSITED AS HEAVY PARTICLES OR "EXHAUST WATER" ON ROAD SURFACE
WASH-OFF FROM SURFACES
SPECTRUM OF LEAD-BEARING AIRBORNE AEROSOL PARTICLES
LARGE
SMALL
DRY FALLOUT; SHORT-RANGE TURBULENT TRANSPORT
SHORT- AND LONG-RANGE DIFFUSION IN ATMOSPHERE
WASHOUT BY SCAVENGING BELOW CLOUDS
RAINOUT IN CLOUDS, INCL. NUCLEATION
LEAD IN PRECIPITATION
UPTAKE BY PLANTS
DECOMPOSITION OF PLANTS
RE-INJECTION INTO ATMOSPHERE BY STRONG WINDS
DRY DEPOSITION ON SOIL AND PLANT SURFACES
ATMOSPHERIC PARAMETERS
SPECTRUM OF ATMOSPHERIC TURBULENCE
DIFFUSION CLIMATOLOGY OF INDIVIDUAL SITES; FREQUENCY OF WEAK AND STRONG WINDS
PRECIPITATION FORMS AND AMOUNTS
SINKS:
VEGETATION
SOIL RETENTION
GROUND WATER
RIVER RUNOFF

Figure 2

Model for Flow of Traffic Exhaust Through Environment

✓

and washoff from surfaces appear to be major factors in causing peculiarly high lead concentrations in topsoil along the median strip and immediately east of I-25 at one of our field sites. Special sampling techniques still under development will be necessary before quantitative estimates of strong wind and washoff effects can be made.

B. Meteorological Measurements and Air Sampling

The approach to characterizing movement of lead from traffic exhaust through the atmosphere is to measure the space and time dependence of atmospheric lead levels near a highway in conjunction with simultaneous measurement of wind speed and direction and temperature lapse rate. Concurrent measurement of all atmospheric parameters is necessary to use existing diffusion theory for lead. Application of the existing diffusion theory is restricted to description of the component which travels as a gas, however. Additional measurements of lead particle settling velocity distribution as a function of distance from the highway are also needed to correlate with measured fallout patterns and hence measured soil accumulation patterns. Since existing diffusion theory does consider a wide range of atmospheric stability conditions, the measurements will be of considerable general utility. Thus the measurements will hopefully enable us to develop a fairly general approach for describing particulate transport, and the measurements will also enable us to test this model under a variety of atmospheric and meteorological conditions. Later work will enable us to include washout and precipitation runoff. The meteorological data will also be used for the effort to couple atmospheric dispersion with soil uptake and accumulation.

The theoretical basis for the meteorological measurements was given first by Sutton (1949) and later by Pasquill (1962) in a form often used for field measurements. Measurement of wind direction and velocity as a function of time enables calculation of the variance in each of the wind components. These quantities are then used in the Pasquill diffusion equation which, providing the source strength is known, can be used to predict the downstream dilution of a pollutant whose movement can be characterized by gaseous transport equations. The temperature lapse rate strongly affects the atmospheric stability, and its measurement enables the stability conditions to be classified in one of several broad categories. This approach has been used with success for describing atmospheric dispersion of radioactive pollutants (Reiter, 1963, 1965).

C. Instrumentation and Meteorological Measurements

1. Bivane Anemometers

Wind speed and direction are measured by means of four bivane anemometers obtained from the R. M. Young Co. These instruments are shown deployed for a field calibration in Figure 3. A close-up view of a sensing unit is shown in Figure 4. The anemometer affixed to a portable mast deployed under field conditions is shown in Figure 5. Agreement of measured speeds is within ±0.1 m/sec when average values over ten minute periods are considered. Azimuth readings agree within approximately 1°, e.g., the accuracy to which units may be oriented with reference to a geographic coordinate system. Elevation angles tend to average 0°

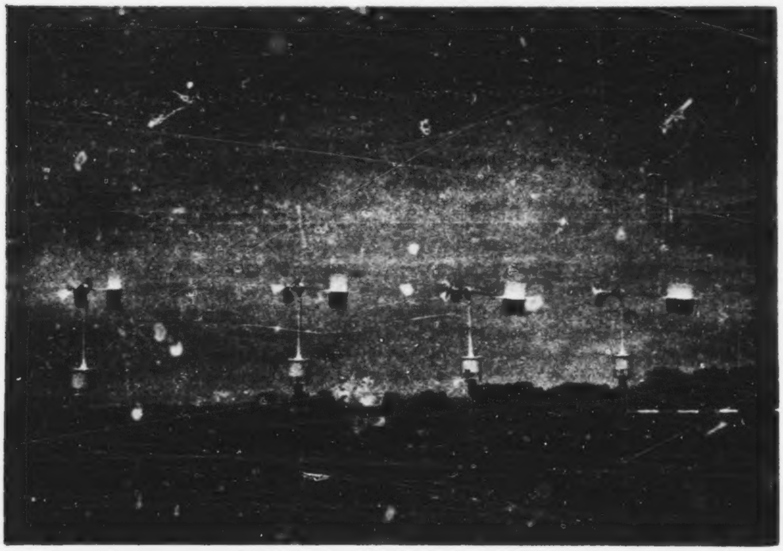


Figure 3

Reproduced from best available copy.

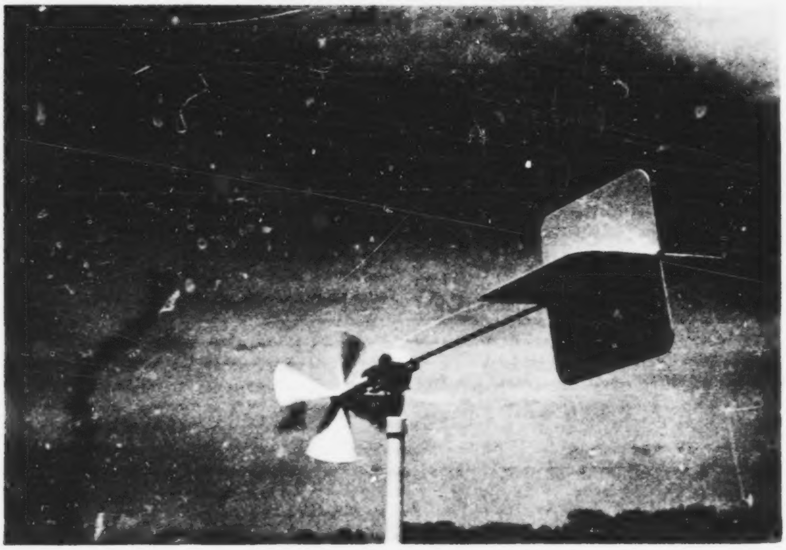


Figure 4

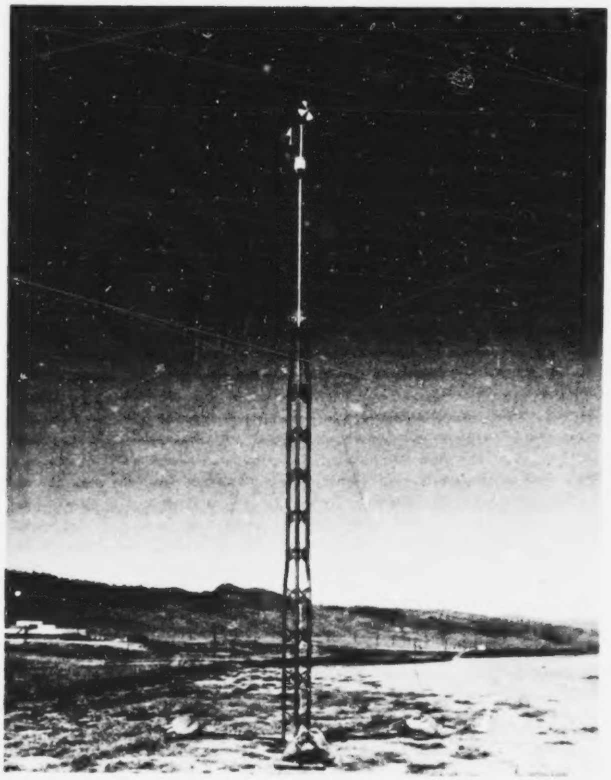


Figure 5

within 1° during a ten minute calibration run on level terrain.

The bivane anemometry is designed for use in mobile field units. However, the azimuth and elevation angle calibrations can change when the anemometers are moved from one location to another. Computer programs have been developed to facilitate quick checks on the internal consistency of wind data received from the four units. These data are mean standard deviation values for wind speeds and directions over

Reproduced from best available copy.

specified time periods. Samples of calibration printouts from the Colorado State University CDC 6400 computer are shown in Table V. The computer programs also facilitate correction of wind data with respect to an assigned true wind direction. While this correction will normally not be necessary, a possibility of maladjustment in one or more of the instruments would require this correction. Such a maladjustment would be detected from the computer printout described above. The second correcting program was deemed necessary since minor maladjustments of the instruments would normally not be detected until after the field experiments were completed. The correction program thus allows full use of the acquired data in the event of such a maladjustment.

2. Platinum Resistance Thermometry

The technique for determining the atmospheric lapse rate is to measure the temperature profile using multiple platinum resistance thermometers mounted on a fifty-foot collapsible mast. When collapsed, the mast can be transported on the truck trailer shown in Figure 6. The mast is erected by means of the winch arrangement shown in operation in Figure 7. The fully extended mast is shown in Figure 8. The arrangement developed allows measurement of temperature differences within ±0.01°C.

3. Recording Equipment

Electrical output from sensing instrumentation is recorded on a 20-channel Brush digital magnetic tape recorder. Each channel may be scanned as rapidly as every 0.4 second. Tapes are wound in self-contained cartridges which facilitate rapid tape change and easy storage. Data

```
06/08/71                    ANALYSIS OF BRUSH RECORDER TAPES.          PAGE NO.  4
                  FIELD AT ATMOSPHERIC SCIENCE-EQUIPMENT CHECK OUT
                  6-7-71

                                                                                     3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 20

START TIME: 161000  END TIME: 161922  TIME INTERVAL:   1000  CHANNELS:   X  X  X  X  X  X  X  X  X  X  X  X  X  X  X  X  X  X
                                                                    S1 D1 S2 D2    S3 D3 S4 D4    T1 E1 T2 E2 E3 T3 E4 T4
CHANNEL  3  MEAN =     2.481  DEVIATION =      .981
CHANNEL  4  MEAN =   128.482  DEVIATION =    32.297
CHANNEL  5  MEAN =     2.271  DEVIATION =      .893
CHANNEL  6  MEAN =   129.864  DEVIATION =    31.874
CHANNEL  7  MEAN =     0.000  DEVIATION =     0.000
CHANNEL  8  MEAN =     2.444  DEVIATION =      .930
CHANNEL  9  MEAN =   116.390  DEVIATION =    28.414
CHANNEL 10  MEAN =     2.447  DEVIATION =      .915
CHANNEL 11  MEAN =   129.585  DEVIATION =    31.979
CHANNEL 12  MEAN =     0.000  DEVIATION =     0.000
CHANNEL 13  MEAN =     0.000  DEVIATION =     0.000
CHANNEL 14  MEAN =     -.186  DEVIATION =     7.991
CHANNEL 15  MEAN =     0.000  DEVIATION =     0.000
CHANNEL 16  MEAN =     -.520  DEVIATION =     8.142
CHANNEL 17  MEAN =     -.858  DEVIATION =     7.435
CHANNEL 18  MEAN =     0.000  DEVIATION =     0.000
CHANNEL 19  MEAN =      .506  DEVIATION =     7.999
CHANNEL 20  MEAN =     0.000  DEVIATION =     0.000
NO. OF POINTS USED IS 128.
```

TABLE V

Analysis of 9 min 22 sec of data taken during an equipment checkout. Right side of printout shows tape recorder channel locations of the various parameters: S = speed, D = azimuth, E = elevation, T = temperature; numbers indicate the instrument. Left hand side shows start and stop time of interval and approximate time interval. Mean and standard deviation for the time interval are given for each instrument. Channels 3, 5, 8, 10 give the average speed and standard deviation in m sec^{-1} of instruments 1, 2, 3, and 4, respectively. Similarly, channels 4, 6, 9, 11 give the azimuthal direction in degrees and channels 14, 16, 17, 19 give the elevation angle of instruments 1, 2, 3, and 4, respectively. Note that the temperatures were not calculated and that channel 9 differs from 4, 6, and 11 due to a directional misalignment of that instrument.

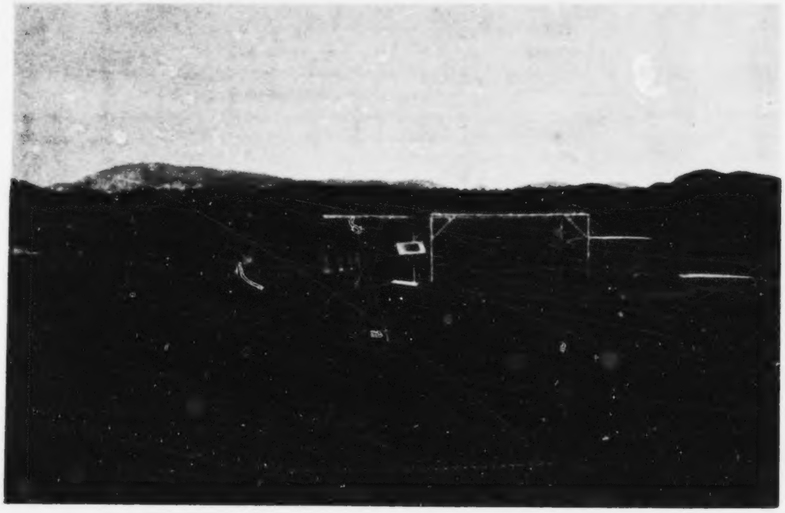


Figure 6

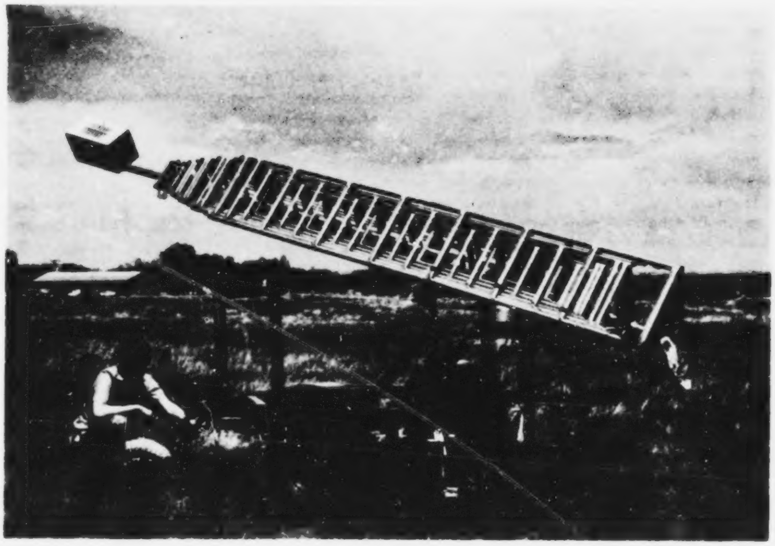


Figure 7

Figure 8

from cartridges are transferred onto computer-compatible tape using a Metrodata Systems 620 reader. The recorder unit is shown on the left in Figure 9. The computer program allows us to print every tenth scan of all channels for a quick check on the quality of recorded measurements before data are subjected to further processing. Table VI is a partial printout of actual millivolt data. In Table VII a partial printout of the millivolt data as recorded on magnetic tape is given; provision is also made for conversion of raw data into the engineering units in Table VIII.

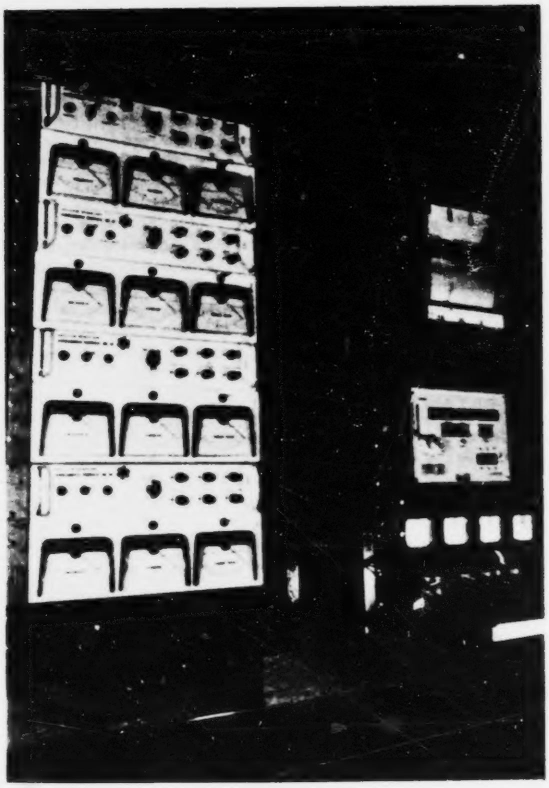


Figure 9

```
PRELIMINARY DUMP OF BRUSH TAPE.  ALL READINGS IN MILLIVOLTS.   06/07/71                PAGE NO.   8
FIELD AT ATMOSPHERIC SCIENCE-EQUIPMENT CHECK OUT
6-7-71

                                                       CHANNEL NUMBER
  TIME           3     4     5     6     7     8     9    10    11    12    13    14    15    16    17    18    19    20

16.03.16       +071  +422  +093  +408  +000  +098  +407  +091  +399  +000  +000  +484  +000  +491  +470  +000  +475  +000
16.03.21       +091  +415  +104  +427  +000  +105  +418  +099  +400  +000  +000  +538  +000  +485  +447  +000  +491  +000
16.03.26       +079  +397  +088  +406  +000  +097  +418  +088  +408  +000  +000  +475  +000  +520  +481  +000  +453  +000
16.03.30       +094  +346  +075  +329  +000  +069  +323  +065  +383  +000  +000  +416  +000  +503  +536  +000  +605  +000
16.03.35       +067  +399  +076  +391  +000  +066  +384  +056  +385  +000  +000  +579  +000  +471  +519  +000  +510  +000
16.03.40       +050  +328  +059  +350  +000  +071  +374  +062  +388  +000  +000  +491  +000  +343  +494  +000  +669  +000
16.03.44       +074  +370  +054  +397  +000  +048  +356  +057  +365  +000  +000  +504  +000  +532  +578  +000  +533  +000
16.03.49       +059  +409  +073  +399  +000  +078  +377  +080  +350  +000  +000  +474  +000  +433  +463  +000  +459  +000
16.03.54       +092  +393  +090  +371  +000  +043  +393  +087  +382  +000  +000  +351  +000  +486  +465  +000  +474  +000
16.03.58       +084  +354  +086  +359  +000  +090  +355  +087  +367  +000  +000  +526  +000  +501  +453  +000  +443  +000
16.04.03       +057  +371  +067  +356  +000  +074  +354  +063  +381  +000  +000  +546  +000  +498  +472  +000  +435  +000
16.04.08       +051  +374  +072  +396  +000  +073  +343  +084  +355  +000  +000  +587  +000  +522  +446  +000  +455  +000
16.04.12       +081  +309  +051  +280  +000  +063  +328  +068  +358  +000  +000  +448  +000  +646  +580  +000  +492  +000
16.04.17       +040  +313  +039  +356  +000  +062  +326  +092  +325  +000  +000  +553  +000  +541  +391  +000  +431  +000
16.04.22       +058  +320  +063  +318  +000  +063  +327  +068  +334  +000  +000  +548  +000  +498  +498  +000  +442  +000
16.04.26       +048  +362  +050  +376  +000  +054  +314  +054  +322  +000  +000  +517  +000  +437  +468  +000  +464  +000
16.04.31       +074  +331  +042  +314  +000  +043  +365  +055  +351  +000  +000  +507  +000  +567  +572  +000  +535  +000
16.04.36       +053  +364  +045  +339  +000  +064  +343  +053  +338  +000  +000  +633  +000  +493  +497  +000  +532  +000
16.04.40       +075  +383  +064  +416  +000  +060  +356  +056  +341  +000  +000  +470  +000  +405  +482  +000  +473  +000
16.04.45       +086  +377  +073  +382  +000  +075  +380  +063  +366  +000  +000  +468  +000  +461  +405  +000  +480  +000
16.04.50       +059  +354  +062  +417  +000  +040  +368  +073  +389  +000  +000  +490  +000  +483  +467  +000  +433  +000
16.04.54       +072  +390  +074  +389  +000  +065  +358  +070  +401  +000  +000  +538  +000  +449  +567  +000  +532  +000
                                                                             +481  +000  +401  +417  +000  +480  +000
                                                                             +438  +000  +505  +458  +000  +461  +000
                                                                             +494  +000  +458  +429  +000  +562  +000
                                                                             +433  +000  +535  +563  +000  +513  +000
                                                                             +522  +000  +461  +410  +000  +448  +000
                                                                             +483  +000  +482  +479  +000  +478  +000
                                                                             +505  +000  +453  +428  +000  +539  +000
                                                                             +571  +000  +599  +494  +000  +456  +000
                                                                             +611  +000  +587  +437  +000  +509  +000
                                                                             +665  +000  +502  +487  +000  +486  +000
                                                                             +528  +000  +496  +536  +000  +547  +000
                                                                             +436  +000  +585  +435  +000  +389  +000
                                                                             +463  +000  +478  +644  +000  +588  +000
                                                                             +500  +000  +407  +456  +000  +522  +000
                                                                             +376  +000  +480  +327  +000  +403  +000
                                                                             +512  +000  +611  +504  +000  +606  +000
                                                                             +442  +000  +574  +497  +000  +554  +000
                                                                             +760  +000  +560  +662  +000  +814  +000
                                                                             +427  +000  +454  +385  +000  +505  +000
                                                                             +406  +000  +635  +458  +000  +454  +000
                                                                             +676  +000  +570  +586  +000  +406  +000
                                                                             +527  +000  +542  +477  +000  +496  +000
                                                                             +542  +000  +436  +351  +000  +400  +000
                                                                             +578  +000  +629  +560  +000  +553  +000
                                                                             +485  +000  +490  +446  +000  +428  +000
                                                                             +508  +000  +602  +462  +000  +506  +000
                                                                             +466  +000  +520  +473  +000  +336  +000
                                                                             +479  +000  +439  +433  +000  +439  +000
                                                                             +461  +000  +502  +410  +000  +439  +000
                                                                             +465  +000  +464  +494  +000  +427  +000
                                                                             +564  +000  +456  +463  +000  +540  +000
                                                                             +536  +000  +473  +427  +000  +443  +000
                                                                             +578  +000  +512  +488  +000  +431  +000
16.07.33       +034  +306  +029  +298  +000  +032  +280  +036  +288  +000  +000  +444  +000  +446  +475  +000  +563  +000
```

TABLE VI

Shows partial preliminary printout of actual millivolt data. Every tenth scan of the data on the magnetic tape is printed out. Total wind speeds are on channels 3, 5, 8, 10, azimuthal direction on channels 4, 6, 9, 11, and elevation angle on channels 14, 16, 17, 19 of instruments 1, 2, 3, and 4, respectively.

```
              DUMP OF BRUSH TAPE.  ALL READINGS IN MILLIVOLTS.   05/07/71                        PAGE NO. 141

05/07/71  FOUR ANEMOMETER CHECK OUT AT CHRISTMAN FIELD.

                                                                  CHANNEL NUMBER
  TIME           3     4     5     6     7     8     9    10    11    12    13    14    15    16    17    18    19    20

14.17.20       +074  +558  +080  +524  +000  +088  +635  +092  +618  +990  +638  +581  +636  +496  +274  +633  +330  +608
14.17.20       +080  +542  +081  +521  +000  +087  +635  +091  +617  +990  +638  +531  +636  +503  +271  +633  +346  +609
14.17.21       +086  +519  +085  +538  +000  +085  +626  +096  +614  +990  +638  +525  +637  +471  +274  +632  +328  +610
14.17.21       +085  +541  +085  +540  +000  +086  +617  +095  +616  +990  +637  +519  +637  +469  +271  +632  +278  +610
14.17.22       +089  +554  +083  +527  +000  +085  +633  +092  +619  +990  +637  +501  +638  +465  +243  +632  +338  +611
14.17.22       +089  +540  +083  +543  +000  +081  +638  +090  +629  +990  +636  +491  +638  +438  +255  +632  +372  +611
14.17.22       +084  +538  +064  +551  +000  +084  +646  +087  +623  +990  +636  +458  +639  +440  +254  +631  +374  +611
14.17.23       +090  +555  +093  +547  +000  +083  +626  +091  +624  +990  +636  +455  +639  +440  +256  +631  +313  +611
14.17.23       +092  +546  +088  +536  +000  +075  +633  +092  +623  +990  +636  +468  +639  +439  +264  +631  +334  +611
14.17.24       +091  +544  +083  +549  +000  +080  +638  +090  +624  +990  +636  +453  +639  +486  +269  +631  +358  +611
14.17.25       +093  +558  +086  +533  +000  +086  +619  +091  +591  +990  +635  +509  +639  +491  +260  +632  +319  +611
14.17.25       +093  +545  +065  +519  +000  +085  +609  +088  +588  +990  +635  +528  +640  +463  +267  +632  +335  +611
14.17.25       +088  +523  +082  +521  +000  +089  +604  +091  +586  +989  +635  +532  +640  +456  +267  +633  +337  +611
14.17.26       +088  +527  +084  +516  +000  +095  +601  +088  +586  +990  +636  +509  +640  +483  +262  +633  +340  +610
14.17.26       +092  +524  +087  +509  +000  +094  +604  +086  +586  +990  +636  +524  +640  +457  +258  +634  +319  +610
14.17.27       +094  +520  +086  +513  +000  +091  +606  +082  +590  +990  +636  +498  +640  +433  +250  +634  +302  +610
14.17.27       +094  +524  +082  +513  +000  +088  +609  +078  +591  +990  +637  +480  +639  +438  +251  +634  +327  +609
14.17.27       +092  +523  +080  +517  +000  +086  +610  +076  +591  +990  +637  +487  +639  +432  +258  +635  +359  +609
14.17.28       +089  +529  +078  +514  +000  +084  +610  +075  +590  +990  +637  +480  +639  +454  +259  +635  +367  +609
14.17.28       +087  +528  +075  +516  +000  +084  +606  +074  +591  +990  +637  +486  +639  +464  +262  +635  +376  +609
                                                                             +527  +639  +501  +275  +635  +370  +609
                                                                             +538  +638  +508  +271  +635  +362  +608
                                                                             +552  +638  +475  +263  +635  +343  +608
                                                                             +531  +638  +448  +263  +635  +332  +608
                                                                             +511  +637  +453  +262  +635  +316  +608
                                                                             +490  +637  +455  +257  +635  +315  +607
                                                                             +491  +637  +427  +262  +635  +305  +607
                                                                             +486  +636  +458  +259  +635  +337  +607
                                                                             +515  +636  +452  +260  +635  +337  +607
                                                                             +509  +636  +445  +264  +635  +350  +607
                                                                             +500  +636  +452  +244  +634  +303  +608
                                                                             +499  +636  +419  +244  +634  +302  +608
                                                                             +476  +636  +415  +242  +633  +306  +609
                                                                             +461  +636  +418  +241  +633  +287  +609
                                                                             +460  +636  +413  +239  +633  +289  +609
                                                                             +463  +636  +415  +234  +632  +304  +609
                                                                             +469  +636  +408  +240  +632  +330  +610
                                                                             +467  +637  +421  +246  +632  +339  +610
                                                                             +473  +637  +466  +245  +632  +329  +610
                                                                             +515  +637  +468  +240  +632  +308  +610
                                                                             +540  +637  +455  +233  +631  +172  +610
                                                                             +497  +637  +419  +228  +631  +322  +610
                                                                             +480  +638  +417  +232  +631  +400  +611
                                                                             +489  +638  +420  +243  +631  +401  +611
                                                                             +484  +638  +451  +233  +631  +410  +611
                                                                             +479  +638  +459  +251  +631  +414  +611
                                                                             +499  +638  +490  +251  +631  +401  +610
                                                                             +549  +639  +470  +254  +631  +415  +610
                                                                             +518  +639  +474  +259  +632  +409  +610
                                                                             +509  +638  +505  +264  +633  +410  +609
                                                                             +564  +638  +492  +262  +634  +345  +608
                                                                             +548  +637  +456  +267  +634  +333  +607
                                                                             +497  +636  +482  +267  +634  +339  +607
14.17.44       +096  +546  +081  +518  +000  +093  +635  +086  +615  +990  +638  +525  +636  +487  +288  +634  +346  +607
```

TABLE VII

Partial printout of actual millivolt data as recorded on magnetic tape. Channels 3, 5, 8, 10 are total wind speed, channels 4, 6, 9, 11 are azimuthal direction, channels 14, 16, 17, 19 are elevation, and channels 13, 15, 18, 20 are temperature of instruments 1, 2, 3, and 4, respectively.

```
04/14/71          ENGINEERING UNIT CONVERSION FOR CHANNELS 1 - 20.                                     PAGE NO.  6
         03/11/71 MEASUREMENTS MADE IN PARKING LOT OF ATMOSPHERIC SCIENCE BUILDING.
         MADE BY GARY COBB.                                                  D. MC.
 TIME       3      4      5      6      7      8      9     10     11     12     13     14     15     16     17     18     19     20
112219    2.2   74.1    2.1   83.2    0.0    2.5   87.4    2.6   90.1    0.0    2.2    9.9    2.2   37.5     .7    2.5   -7.0    2.6
112219    2.0   79.9    2.3   82.4    0.0    2.5   85.5    2.6   89.4    0.0    1.9   10.2    2.4   33.4   -1.5    2.6   -8.1    2.6
112220    1.8   83.5    2.2   85.5    0.0    2.6   86.6    2.5   88.6    0.0    1.8   11.0    2.2   28.7   -2.5    2.5   -7.2    2.6
112220    1.8   83.9    2.3   76.8    0.0    2.6   87.0    2.8   88.2    0.0    1.8   16.5    2.3   32.5   -2.6    2.6   -4.3    2.7
112221    2.0   81.9    2.2   70.5    0.0    2.7   85.5    2.9   90.9    0.0    2.3   20.9    2.3   35.9   -2.1    2.8   -3.6    2.9
112222    2.4   64.6    2.4   73.8    0.0    2.7   84.4    3.0   87.4    0.0    2.3   25.9    2.4   35.7    1.8    2.7   -1.7    3.0
112222    2.3   58.4    2.4   75.0    0.0    2.6   84.4    2.9   87.8    0.0    2.3   33.9    2.4   40.3    2.3    2.5   -1.8    2.9
112222    2.2   55.5    2.3   73.1    0.0    2.5   82.6    2.9   89.8    0.0    2.3   29.4    2.3   44.6    4.0    2.4   -1.2    2.8
112223    2.3   59.9    2.2   73.1    0.0    2.4   82.6    2.8   85.9    0.0    2.2   18.7    2.1   47.4    7.8    2.5    -.3    2.8
112223    2.2   57.7    2.1   67.9    0.0    2.5   78.1    2.8   79.5    0.0    2.1   13.7    2.1   44.0    7.7    2.4   -2.1    2.7
112224    2.0   51.2    1.9   66.1    0.0    2.4   71.5    2.8   76.5    0.0    2.1   13.8    1.9   41.4    4.9    2.4   -2.7    2.7
112224    2.2   48.0    2.0   61.7    0.0    2.5   66.4    2.5   77.6    0.0    2.5   19.4    2.1   41.5    2.6    2.5    1.7    2.5
112224    2.6   39.9    2.0   52.5    0.0    2.5   60.8    2.5   71.4    0.0    2.6   28.0    2.0   43.2    2.2    2.5    5.9    2.4
112225    2.5   47.6    2.1   43.2    0.0    2.4   68.9    2.4   72.8    0.0    2.5   20.5    2.1  -45.2    2.1    2.2    8.0    2.3
112225    2.7   59.9    2.0   51.8    0.0    2.0   74.8    2.3   81.0    0.0    2.8    7.8    2.0  -52.3    6.4    1.8    8.8    2.3
112226    2.7   50.5    2.2   64.6    0.0    1.9   61.6    2.1   83.6    0.0    2.7    1.1    2.3   22.9    8.1    2.0   11.8    2.2
112227    2.6   64.3    2.3   62.1    0.0    2.0   65.2    2.1   81.0    0.0    2.5    6.4    2.4   23.2    2.7    2.0    9.2    2.0
112227    2.6   71.8    2.5   62.8    0.0    2.0   69.3    1.9   79.9    0.0    2.6    6.0    2.4   32.7    -.5    2.0     .3    2.0
112227    2.5   66.5    2.4   66.8    0.0    2.1   71.9    1.9   79.5    0.0    2.3   -1.2    2.3   36.2    -.0    2.1   -2.9    1.9
112228    2.1   65.4    2.4   77.6    0.0    2.1   74.1    2.1   79.9    0.0    2.1    4.2    2.5   30.9     .9    2.2    4.4    2.3
112228    2.2   63.2    2.4   85.1    0.0    2.5   83.7    2.4   84.8    0.0    2.3   12.8    2.4   30.7    4.8    2.7   12.0    2.5
112229    2.5   66.9    2.6   77.6    0.0    2.8   81.1    2.5   76.5    0.0    2.8   16.0    2.9   26.2    -.8    2.9    1.5    2.5
112229    3.2   69.5    3.1   66.1    0.0    3.0   69.3    2.8   66.6    0.0    3.4   14.4    3.2   23.5   -4.8    2.9  -10.1    2.9
112230    3.4   70.2    3.2   62.1    0.0    2.9   66.4    2.8   65.1    0.0    3.2   19.6    3.1   26.8   -4.6    2.9   -5.8    2.6
                                                                               .9   18.1    3.0   25.0     .3    2.8    3.8    2.7
                                                                               .6   13.6    2.5   24.2     .2    2.5    -.4    2.5
                                                                               .5   21.4    2.5   32.3   -2.1    2.9    1.4    3.0
                                                                               .5   19.4    2.4   41.8     .5    2.9   -2.0    3.1
                                                                               .2   23.6    2.2   34.6    2.9    2.5   -1.9    3.2
                                                                               .8   38.4    2.0   23.3    8.9    2.8   -6.1    3.3
                                                                               .0   49.2    2.0   22.9    7.5    3.3   -5.5    3.6
                                                                               .3   41.8    2.5   38.4    2.1    3.4   -7.4    3.6
                                                                               .5   24.6    2.7   38.5     .9    3.3   -7.9    3.5
                                                                               .9   -1.0    2.8   11.6   -5.4    3.2   -7.4    3.2
                                                                               .9   -3.2    2.9    8.5   -8.0    3.0   -5.1    2.9
                                                                               .9   16.7    2.9   33.8    1.0    3.0   -4.6    2.9
                                                                               .0   11.5    2.8   21.8     .3    3.0   -5.2    3.0
                                                                               .0    4.1    2.9   16.8   -6.7    3.0  -11.5    2.9
                                                                               .2   11.4    2.7   23.3   -5.9    3.0   -9.7    3.0
                                                                               .9    7.9    2.7   32.2   -4.9    3.2   -6.6    3.1
                                                                               .7    9.6    2.7   34.8   -2.7    3.2   -6.5    3.3
                                                                               .6   12.8    2.4   33.6     .5    3.1   -8.3    3.2
                                                                               .6    9.8    2.4   35.6    1.1    2.9   -5.0    3.0
                                                                               .5   22.2    2.3   37.2    4.0    2.7    1.1    2.5
                                                                               .6   19.5    2.4   39.9    8.1    2.7   11.2    2.7
                                                                               .1    2.9    2.9   21.8   -2.7    2.9   -7.5    3.1
                                                                               .3   15.4    3.1   20.3   -7.0    3.0  -10.3    3.1
                                                                               .3   14.7    3.0   23.1   -7.5    3.2   -8.0    3.0
                                                                               .3    3.9    2.9   27.5   -7.7    3.0   -1.3    2.9
                                                                               .2    -.5    2.7   26.7   -6.2    2.9   -2.0    2.8
                                                                               .2   -1.2    2.7   28.4   -3.2    2.9   -4.9    2.9
                                                                               .2     .9    2.7   22.7   -3.5    3.1   -5.8    3.0
                                                                               .7    7.3    2.8   26.0   -2.7    3.2   -5.6    3.2
                                                                               .7   15.9    2.8   31.1   -4.2    3.1   -7.5    3.2
                                                                               .5   12.8    2.8   34.7   -5.4    3.1  -10.9    3.1
```

TABLE VIII

Partial printout of data as converted into engineering units of m sec^{-1} and degrees from millivolt data. Channels 3 and 13, 5 and 15, 8 and 18, and 10 and 20 are total wind speeds in m sec^{-1}. Channels 4, 6, 9, 11 are azimuthal direction and channels 14, 16, 17, 19 are elevation angle, both given in degrees. These are for instruments 1, 2, 3, and 4, respectively.

4. Mobile Units

The recorder and display consoles shown in Figure 10 are housed in the pickup truck fitted with camper shown in Figure 11. A second truck equipped with a hoist carries the propane powered generator shown in Figure 12. The generator (Figure 13) is deployed downwind from the source during field measurements as an additional precaution even though there would be no lead contamination using propane as a fuel. The trailer which carries the main mast also carries the three portable wind masts shown in Figure 14. The complete assembly is shown in Figure 6.

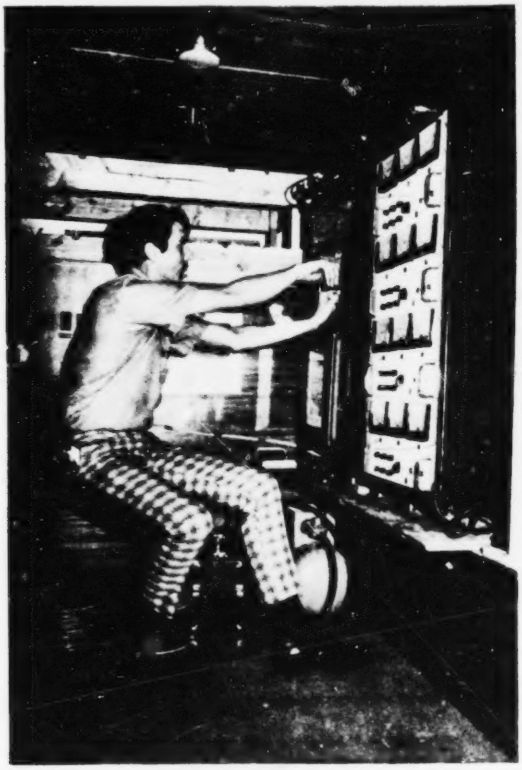


Figure 10

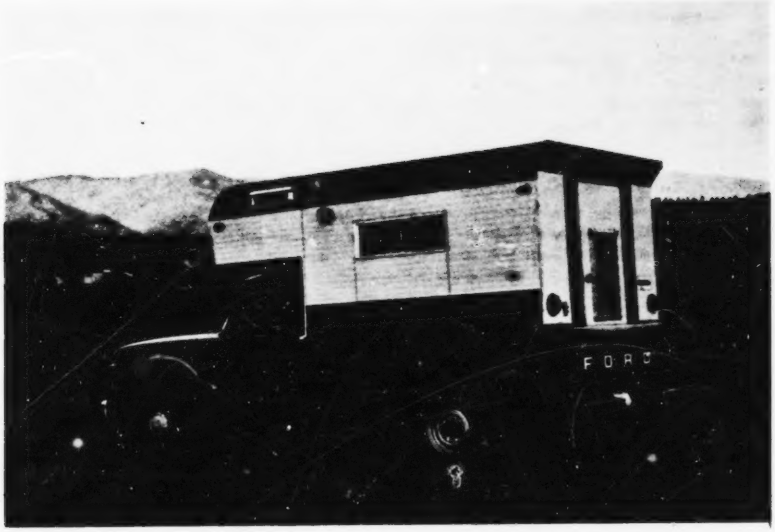


Figure 11

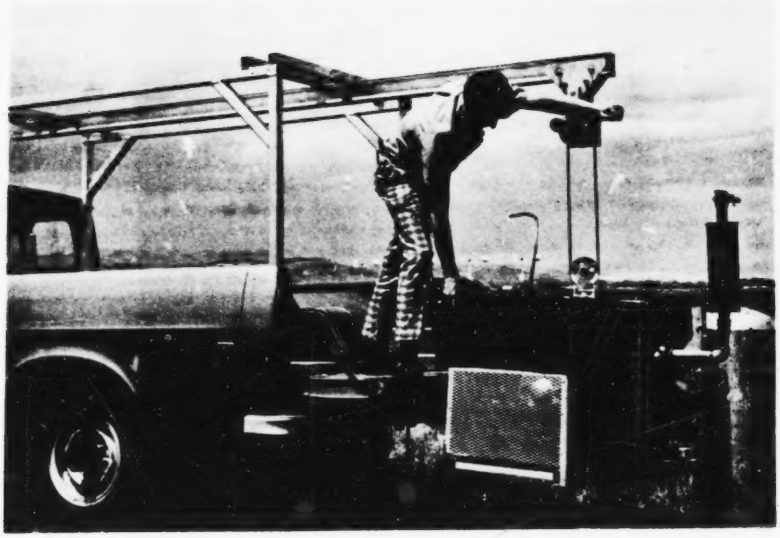


Figure 12

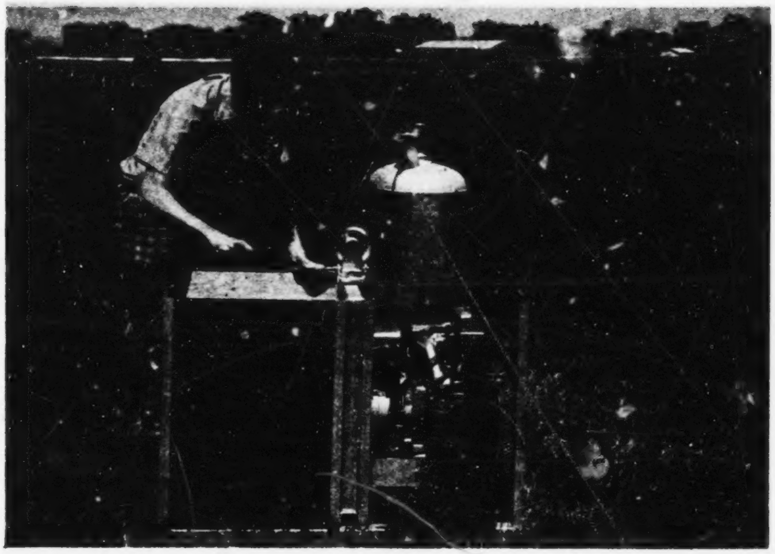


Figure 13

Figure 14

5. Preliminary I-25 Results

The complete mobile measuring system was deployed west of I-25 near the Timnath exit. Prevailing winds during the sampling period were northeasterly, and the source strength was calculated to be 50 μg/m·second on the basis of traffic counts. The observed atmospheric lead concentration decreases with increasing lateral distance from the highway as expected. However, when measured airborne lead concentrations are normalized with respect to that measured at the sampling point closest to the roadway, concentrations for points further away are lower than those predicted on the basis of standard diffusion theory. In other words, standard diffusion theory considerably overestimates airborne lead concentrations. This result is consistent with earlier observations of Besner and Atkins (1970). Continuing work will attempt to determine the extent to which the discrepancy between observed and predicted values can be ascribed to gravitational fallout.

D. Site Selection

Two primary sampling sites along Interstate Highway 25 in Colorado were selected. The two sites are shown on the traffic density map in Figure 15. Numbers on this map are average 24-hour traffic counts based on data obtained from October, 1969, through October, 1970. Details of the site located at the 144th Avenue overpass are shown in Figure 16; there is no traffic exit at this location. A topographic map of the second site, immediately north of the Timnath exit, is shown in Figure 17. The traffic count at the 144th Avenue overpass site is approximately 18,500 vehicles per day, and the traffic count at the site nearer Fort Collins is approximately 8,300 vehicles per day. Factors governing site selection are topography, access to land adjacent to roadway, freedom from interferences due to cross-traffic and frontage roads, and soil composition. While neither primary site is ideal, the two sites afford the research team the opportunity to measure lead transport and accumulation under two quite different traffic density conditions. Site selection is based on collaboration of the participants concerned with meteorology, atmospheric chemistry, transport and accumulation of lead in soil, and uptake of lead in plants and animals.

All sampling programs which involve deployment of equipment close to the edge of the pavement are coordinated with the State of Colorado Department of Highways. Any activity which would obstruct vision or the flow of traffic is ruled out on the basis of motorist safety. In cases where equipment is deployed on State land adjacent to the highway, the State Highway Department is notified at least 24 hours in advance of the deployment. In cases where the equipment is placed on private land, consent of the land owner is obtained. Special efforts are made to acquaint the land owners with the nature and objectives of the CSU project, and questions concerning legal liability are coordinated through the office of the University attorney.

Because both primary sites are several miles from Fort Collins, a third site for pilot experiments was selected along U.S. Highway 287 south of Fort Collins. This site was used to test meteorological and air sampling equipment. The initial site also enabled the team to coordinate various air, soil, and animal trapping techniques for the systems approach. A number of alternate sites are being used to obtain the necessary atmospheric detail very close to the edge of the pavement. It is anticipated that the results obtained for the alternate sites will be directly applicable to the interstate situation. However, it will be necessary to verify this assumption experimentally.

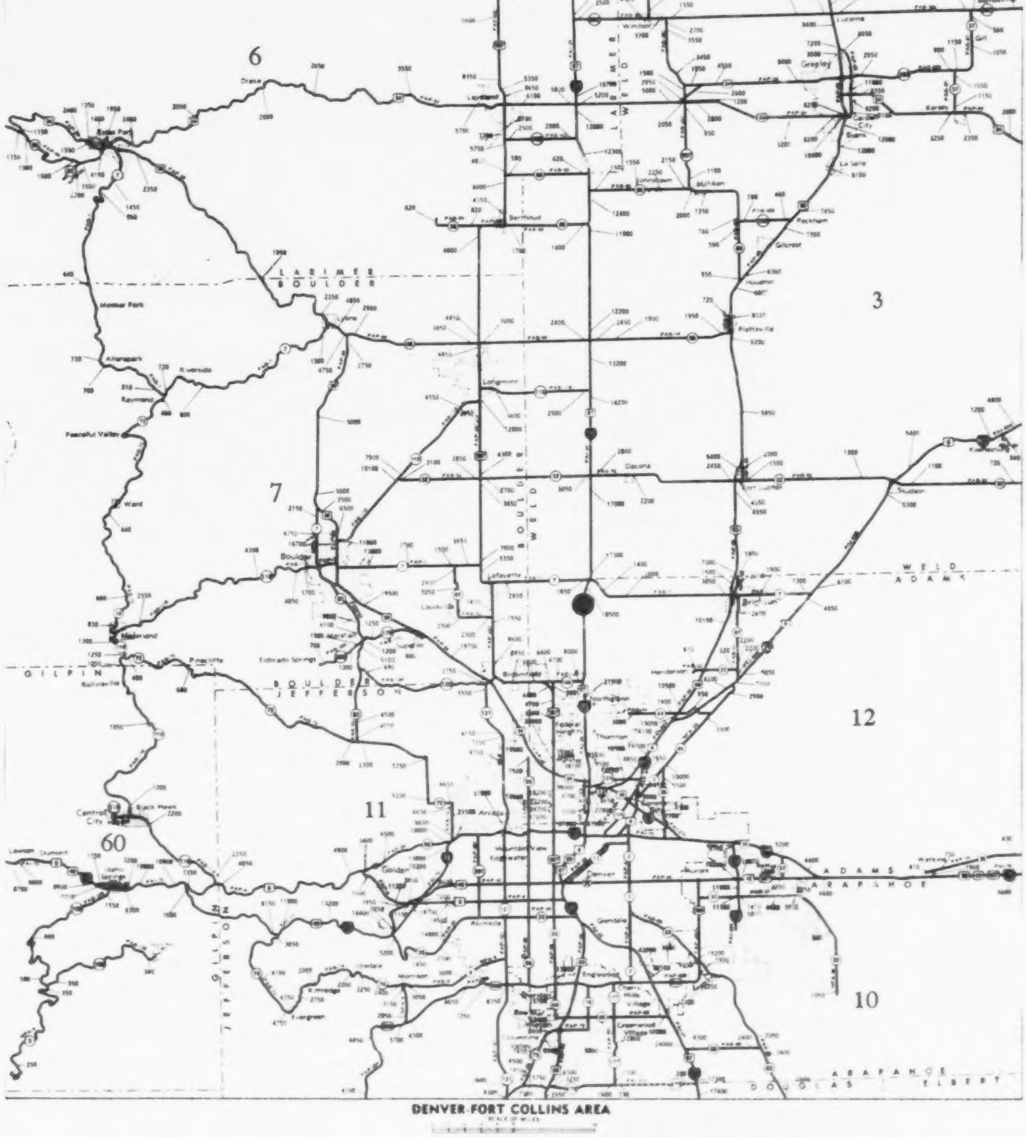
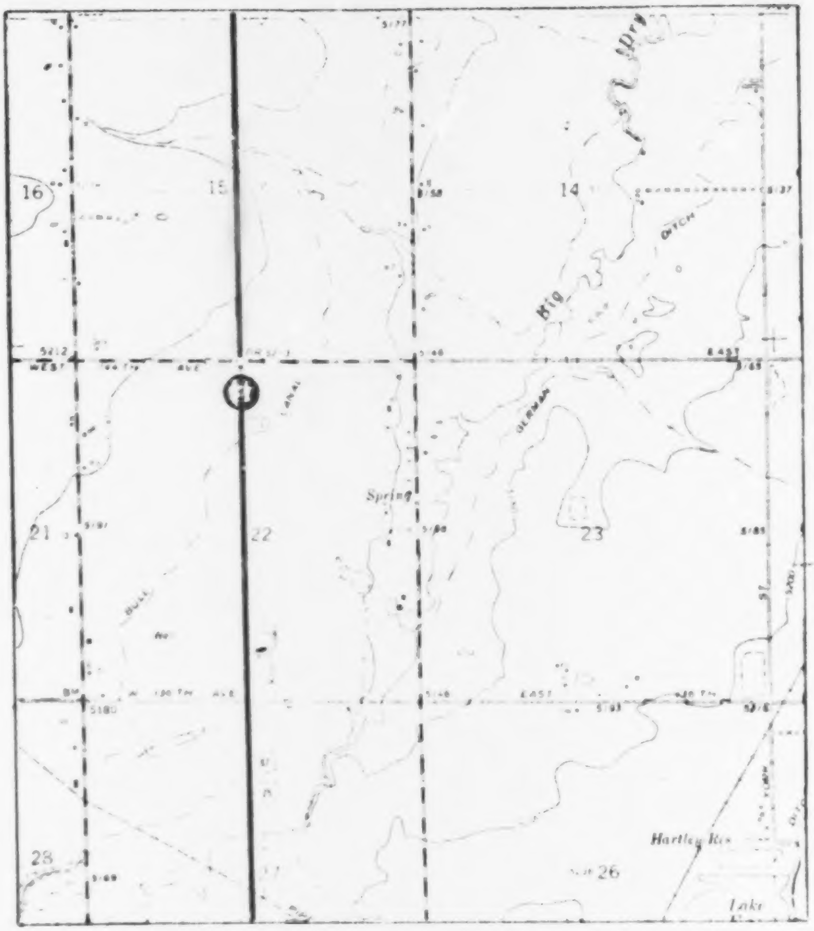

6
7
3
12
11
60
10
Fort Collins
Laporte
Bellvue
Pierce
Ault
Eaton
Lucerne
Barnesville
Gill
Windsor
Greeley
Garden City
Evans
Kersey
La Salle
Loveland
Drake
Estes Park
Johnstown
Milliken
Berthoud
Peckham
Gilcrest
LARIMER
BOULDER
WELD
Meeker Park
Lyons
Platteville
Allenspark
Riverside
Raymond
Peaceful Valley
Longmont
Dacono
Fort Lupton
Hudson
Keenesburg
Ward
Boulder
Lafayette
Louisville
Brighton
ADAMS
Nederland
Eldorado Springs
Broomfield
Henderson
GILPIN
Rollinsville
Pinecliffe
JEFFERSON
Northglenn
Federal Heights
Thornton
Arvada
Black Hawk
Central City
Dumont
Idaho Springs
Golden
Denver
Aurora
Watkins
ARAPAHOE
Glendale
Englewood
Kittredge
Evergreen
Cherry Hills Village
Greenwood Village
DOUGLAS
ELBERT
DENVER-FORT COLLINS AREA
SCALE OF MILES

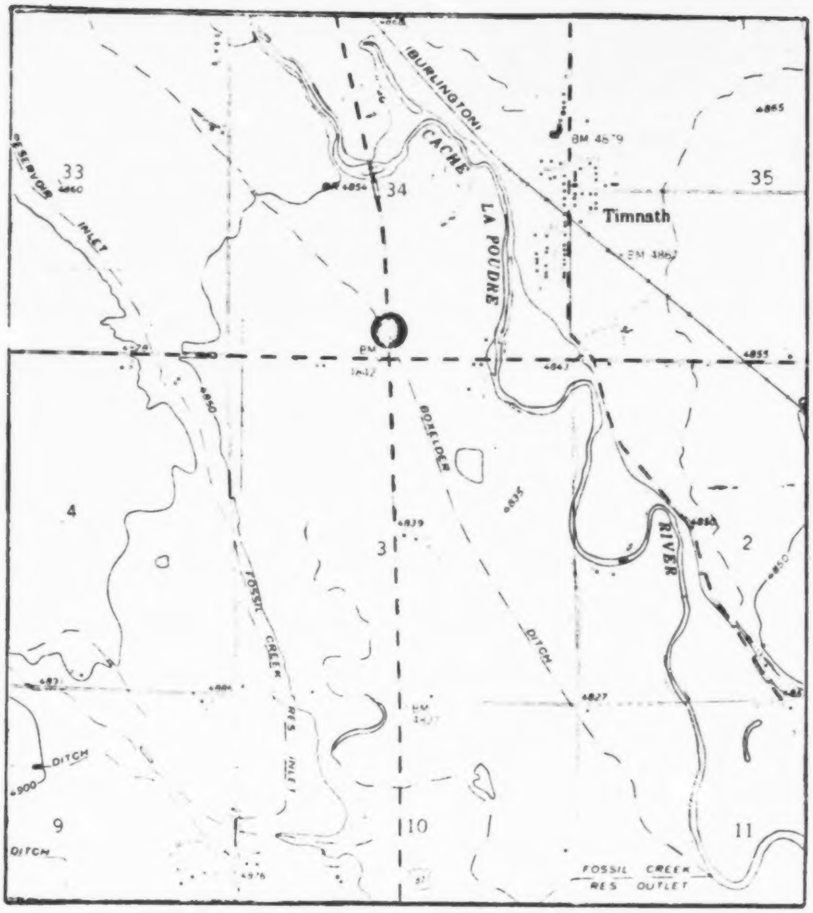
Figure 15


16
15
14
Big Dry
Ditch
Canal
Spring
21
22
23
Bull
28
26
Hartley Res
Lake

144 th Ave. Overpass at Interstate 25 North of Denver, Colorado.

1 mile

Figure 16


(BURLINGTON)
CACHE
LA POUDRE
RIVER
Timnath
BM 4879
BM 4867
RESERVOIR
INLET
FOSSIL CREEK RES. INLET
BOXELDER
DITCH
DITCH
DITCH
FOSSIL CREEK RES OUTLET
33
34
35
4
3
2
9
10
11
4865
4860
4854
4855
BM 4842
4850
4839
4835
4856
4827
BM 4827
4900

Timnath Exit, Interstate 25 East of Fort Collins, Colorado.

1 mile

Figure 17

V. ATMOSPHERIC CHEMISTRY

A. Introduction

Basic information concerning the physical and chemical nature of environmental lead is needed for description of atmospheric transport and accumulation in soils and aqueous systems as well as uptake by plants and animals. Particle settling velocity, which is governed by particle density, size, and geometry, determines the fallout rate in still air. Solubility of atmospheric lead compounds in ground water affects soil uptake. Chemical composition is important in determining possible inadvertent weather modification. While the research tasks described in this section are classified as atmospheric chemistry, there is considerable intermingling of tasks and goals with other program participants.

B. Air Sampling

The standard technique for measuring atmospheric lead employs a high volume air sampler such as the Gelman Instrument Co. Hurricane air sampler which is usually fitted with an 8x10-inch glass-fiber filter. The filter is then analyzed for lead. This is an integrating technique which yields the total amount of lead collected during the sampling period for a given total air throughput. The usual sampling time is 24 hours. It is desired in this study to obtain considerable detail in terms of atmospheric parameters such as wind velocity, turbulence, fallout, and wind direction. As short a sampling time as possible is thus important. A long sampling time would mask the effect of meteorological parameters, and little useful information would be obtained with respect to the validity of any proposed diffusion model.

Thus the sampling period must be made as short as possible consistent with a lead analysis of required precision.

We have found that the standard 8x10-inch glass-fiber filters possess a lead blank measured by atomic absorption spectrometry of 39 μg with a standard deviation of 20 μg. In order to obtain the required accuracy of 5% for the resolution of the distance and meteorological dependence of lead transport, it is thus necessary to collect a 400 μg sample with this technique. Since the lead content at the highway may vary from 1 to 2 $\mu g/m^3$, this would require a total flow of 400 m^3. With the highest available air sampling rate, the sampling time would be 3 hours and 20 minutes. Fifty feet from the highway the lead concentration may drop to a quarter of the value immediately adjacent to the roadway. Sampling time then required would be over 12 hours. The above times are far too long for the present project even though quite satisfactory for routine lead monitoring where values averaged over long periods are sought.

A sampling technique compatible with the short sampling times required for resolution of meteorological parameters has been devised. The technique involves use of the standard high-volume air samplers with a 5-micron Gelman triacetate Metricel filter. The measured collection efficiency of this filter is at least as good as the glass-fiber type-A filter normally employed. The efficiency is also comparable to that of 0.01 μ Metricel filters. Our results are consistent with earlier reports that filters of a given pore size can efficiently collect particles considerably smaller than the specified pore size (Lindeken _et_ _al_., 1964; Megaw _et_ _al_., 1963). Impaction and electrostatic effects may thus be important considerations in the collection mechanism. Additionally, the lead blank on the 5-micron Metricel filter runs about 1.5 μg per 8x10-inch sheet. This requires then at the 5% level a total lead sample of 30 μg. A standard glass-fiber back-up filter is placed behind the 5-micron filter to avoid backstreaming effects and the transfer of lead from the filter screen to the sampling filter. To obtain a 30 μg lead sample the time required for a 1 $\mu g/m^3$ atmospheric concentration is 30 minutes. That for a 0.25 $\mu g/m^3$ atmospheric concentration is 2.0 hours. This is longer than we would like but represents the best compromise available for routine measurements. If the back-up filter is eliminated, with a possible introduction of a 10% error, the sampling time can be reduced to 22 minutes for the 1 $\mu g/m^3$ concentration and 1.5 hours for the 0.25 $\mu g/m^3$ concentration.

In order to determine atmospheric concentrations it is necessary to know the total volume of air passing through the filter as well as the total mass of lead collected. Orifice type flow meters furnished with the high-volume air samplers are not satisfactory without further calibration. A precise ionization type flow meter suitable for high-volume flow rates can be used to calibrate the orifice meters on the commercial samplers.

For additional atmospheric measurements over very short periods of time, we will make use of an aerosol mass analyzer (Olin, 1971). This instrument electrostatically collects atmospheric aerosols on a platinum-plated quartz disc. The lead blank is negligible, and the flow rate is 1 liter/minute. In the absence of a blank, a 10-nanogram quantity of lead is desirable for analysis. The sampling time corresponding to 1 μg of lead per m^3 of air is thus 10 minutes. If we can analyze lead at the two-nanogram level, the sampling time would be two minutes.

C. Gaseous Tracer

Existing theories for the dispersion of a pollutant plume do not treat materials which can either be enhanced or scavenged. It is implied in the applications of such models that pollutants may be treated as molecular species which are not subject to fallout. Thus the theory does not take into account fallout of particulate material in a gravitational field. The extent of this fallout may be estimated by incorporating a gaseous tracer at the source of lead emission. The concentration of this tracer as a function of distance and time may be calculated and compared with observation. The ratio of lead concentration to tracer concentration should decrease with transport distance as fallout occurs. The extent to which fallout occurs can thus be computed.

It is planned to use CO, also a constituent of automobile exhaust, as the gaseous tracer. Selection of a tracer is not a particularly straightforward problem since it is desired to have a substance which diffuses as a molecular species and which is not decomposed or scavenged by environmental processes. While it is known that atmospheric CO is removed by biochemical processes in the soil (Inman et al., 1971), the time scale for this scavenging process is believed to be quite long compared to the time scale for atmospheric dispersion. Air can be collected in evacuated flasks and analyzed for CO in the laboratory using a multireflection infrared cell with a total path length of one meter and a Perkin Elmer Model 337 infrared spectrometer. Another tracing tehcnique which can be considered is determination of atmospheric hydrocarbons resulting from dispersion of unburned hydrocarbons.

D. Characterization of PbBrCl

Lead bromochloride was prepared by heating a mixture of equimolar amounts of lead chloride and lead bromide at 250°C for several hours (Lamb and Niebylski, 1951). The x-ray diffraction pattern shown in Figure 18 was obtained for the material synthesized. Comparison of the diffraction peaks with the values reported in the literature (Julien and Ogilvie, 1960) is made in Table IX. The apparatus shown in Figure 19

TABLE IX

INTERPLANAR SPACING VALUES FOR PbBrCl

Literature Value (1)	Experimental Value	
d(Å)	d(Å)	$I/I_0 \times 100$
2.268	2.30	
2.285	2.28	80
2.421	2.42	
2.547	2.55	
	2.81	
2.824	2.83	
2.995	2.995	
3.63	3.627	100
3.88	3.89	
3.96	3.96	80
4.07	4.08	

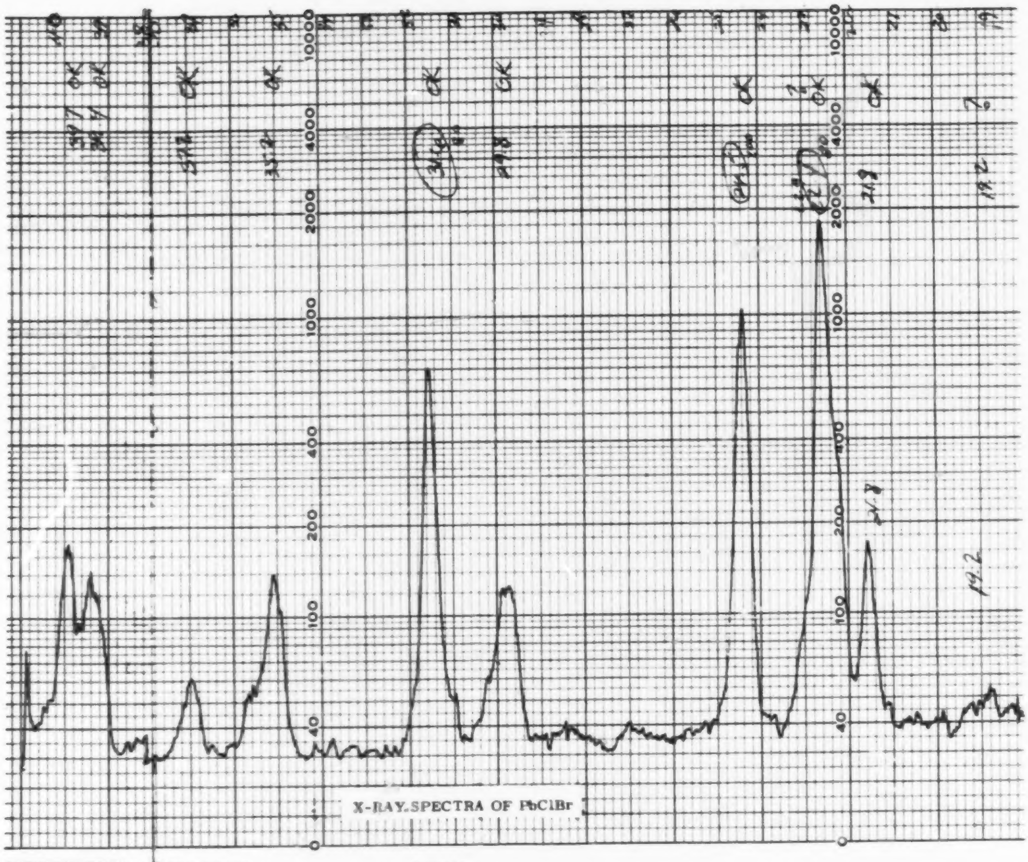

X-RAY SPECTRA OF PbClBr
10000
4000
2000
1000
400
200
100
40
0
OK
OK
OK
OK
OK
OK
OK
OK
21.8
19.2

Figure 18

will be used to measure uptake of hydrocarbon vapors by lead bromochloride as a function of temperature and pressure. The apparatus is a conventional volumetric adsorption system in which the temperature of the adsorption cell is held constant by means of a regulated water bath. Greaseless high-vacuum valves are used throughout. Pressure is measured by means of an MKS Baratron capacitance manometer. It is desired to investigate the nature and extent of interaction between lead bromochloride and unburned hydrocarbons which can appear in exhaust. Formation of condensed hydrocarbon deposits on exhaust particulates has been reported (Moran et al., 1971). Hydrocarbon coatings on lead-bearing exhaust particulates may affect the environmental history of lead.

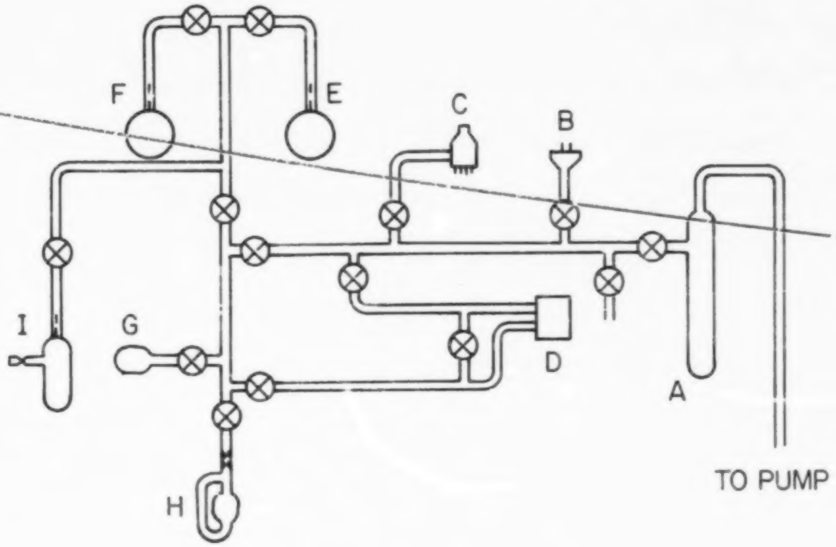
E. Solubility of PbBrCl in Water

A knowledge of the solubility of PbBrCl is of major importance in understanding washout processes in the atmosphere and solution transport of lead through the soil. Solubility of lead bromochloride in water has been measured as a function of temperature. Excess samples of the solid were equilibrated with water at temperatures of 19°C, 33°C, and 43°C. The resulting solutions were analyzed for lead by atomic absorption spectrometry. The analytical results are given in Table X.

TABLE X

SOLUBILITY OF PbBrCl IN WATER

Temperature, °C	Solubility, g Pb/liter
19	0.425
33	0.520
43	0.660



A	LIQUID NITROGEN TRAP
B	THERMOCOUPLE GAUGE
C	IONIZATION GAUGE
D	CAPACITANCE MANOMETER HEAD
E	NITROGEN
F	HELIUM
G	KNOWN VOLUME
H	ADSORBENT
I	ADSORBATE

VOLUMETRIC APPARATUS FOR MEASURING ADSORPTION OF HYDROCARBON VAPOR ON PbBrCl

Figure 19

The logarithm of the solubility is plotted against reciprocal absolute temperature in Figure 20 along with similar data for lead chloride and lead bromide. A question regarding the more stable form of the solid phase arises. The solution undoubtedly contains lead, chloride, and bromide ions. Does the solid phase remain PbBrCl, or is it a mixture of $PbCl_2$ and $PbBr_2$? Two facts argue for the former conclusion: (1) The solubility of the mixed halide is less than that for the bromide or chloride; (2) a plot of the logarithm of the solubility of lead is linear in reciprocal temperature. If this conclusion is correct we can make some calculations.

Consider the following series of reactions:

(1) $PbCl_2(s) = Pb^{+2}(aq) + 2Cl^-(aq) \qquad \Delta G^o = -RT\ln K''_{sp}$

(2) $PbBr_2(s) = Pb^{+2}(aq) + 2Br^-(aq) \qquad \Delta G^o = -RT\ln K'_{sp}$

(3) $PbBrCl(s) = Pb^{+2}(aq) + Cl^-(aq) + Br^-(aq) \qquad \Delta G^o = -RT\ln K_{sp}$

Ideal solution behavior is assumed (solubility products expressed in concentrations rather than activities). K''_{sp} is the solubility product for $PbCl_2$, K'_{sp} that for $PbBr_2$, and K_{sp} that for PbBrCl. If equation (3) is multiplied by two and equations (1) and (2) subtracted from it,

$$2PbBrCl(s) = PbCl_2(s) + PbBr_2(s) \qquad \Delta G^o = -RT\ln(K''_{sp}K'_{sp}/K^2_{sp})$$

we have a measure of the stability of solid PbBrCl toward disproportionation to solid $PbCl_2$ and $PbBr_2$. Calculations have been made at two temperatures, 25°C and 40°C.

The Solubilities of $PbCl_2$, $PbBr_2$ and PbClBr
in Water as a Function of Temperature

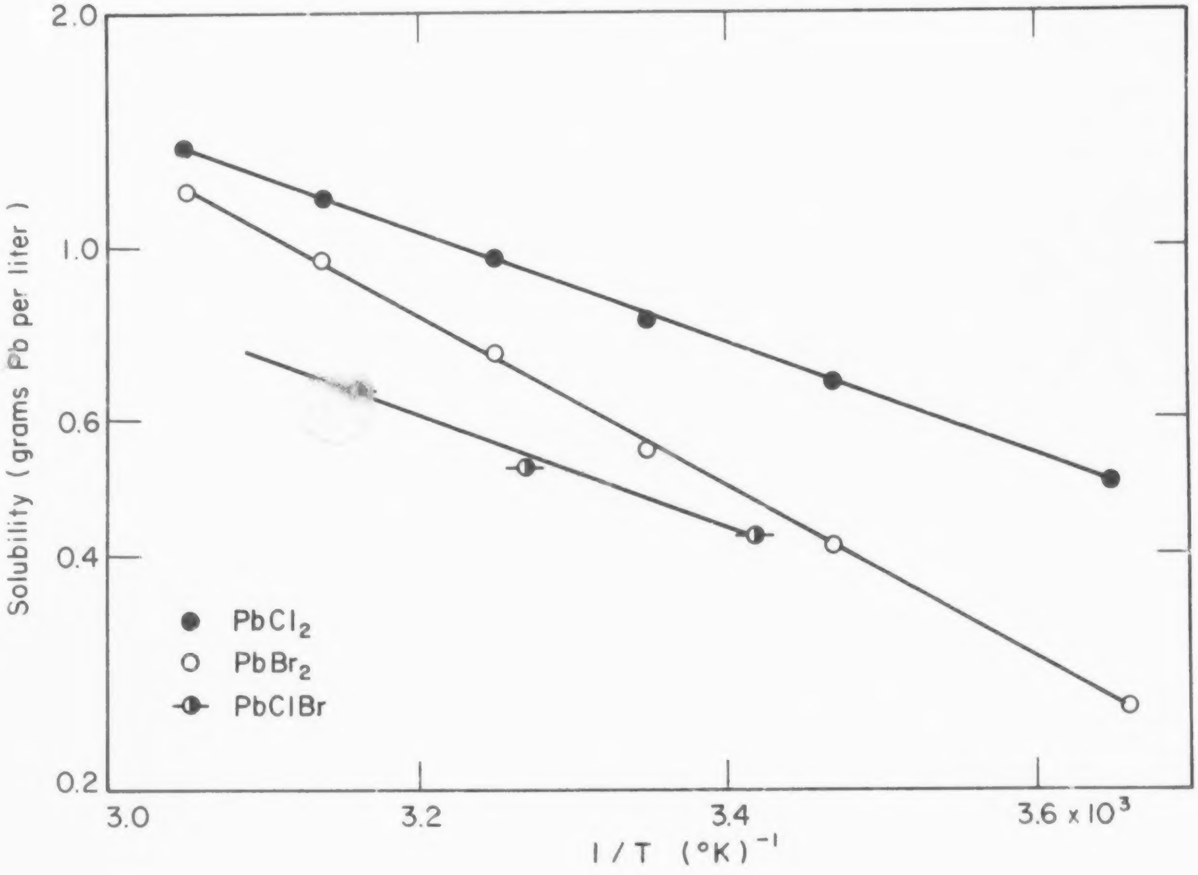


Figure 20

TABLE XI

STABILITY CALCULATIONS FOR PbBrCl

25°C	Sol. (g Pb/l)	Sol. (Moles/l)	K_{sp}
$PbCl_2$	8.05	3.89×10^{-2}	2.35×10^{-4}
$PbBr_2$	5.45	2.64×10^{-2}	7.36×10^{-5}
PbBrCl	4.63	2.24×10^{-2}	4.50×10^{-5}
40°C			
$PbCl_2$	10.3	4.98×10^{-2}	4.94×10^{-4}
$PbBr_2$	8.40	4.05×10^{-2}	2.66×10^{-4}
PbBrCl	6.20	3.00×10^{-2}	1.08×10^{-4}

For the reaction 2 PbBrCl = $PbCl_2$ + $PbBr_2$ (solid)

$\Delta G^o(298°K) = +1.27$ kcal. $\Delta G^o(313°K) = +1.50$ kcal.

Thus PbBrCl is stable toward disproportionation at these two temperatures. It is interesting to extrapolate the solubility data to 0°C and calculate ΔG^o for this temperature. The value is +0.86 kcal. indicating that the stable species is still PbBrCl at the lowest temperature for the existence of aqueous solutions.

It is further possible from this information to calculate the standard free energy of formation at 298°K of PbBrCl. Consider the reactions:

(1) $Pb(s) + Cl_2(g) = PbCl_2(s)$ $\Delta G_f'' = -68.51$ kcal.

(2) $Pb(s) + Br_2(l) = PbBr_2(s)$ $\Delta G_f' = -66.21$ kcal.

(3) $2PbBrCl(s) = PbCl_2(s) + PbBr_2(s)$ $\Delta G = +1.27$ kcal.

If equation (3) is subtracted from the sum of equations (1) and (2)

$$2Pb(s) + Cl_2(g) + Br_2(l) = 2PbBrCl(s)$$

$$\Delta G = -68.51 - 66.21 - 1.27 = -135.99 \text{ kcal.}$$

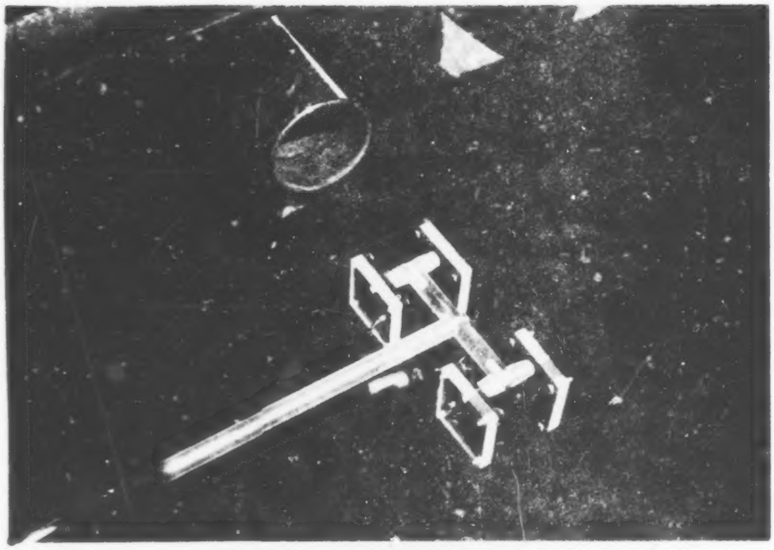
But this is twice the standard free energy of formation of PbBrCl at 298°K as defined by the equation

$$Pb(s) + \tfrac{1}{2}Cl_2(g) + \tfrac{1}{2}Br_2(l) = PbBrCl(s)$$

and thus the standard free energy of formation of PbBrCl at 298°K is -68.00 kcal. Note that $PbCl_2(s)$ is more stable than the mixed halide, but the mixed halide is more stable than a 1:1 molar mixture of the solid $PbCl_2$ and $PbBr_2$.

F. Electrostatic Experiments

A simple electrostatic collector was constructed for deposition of exhaust-containing particles. Parallel tantalum plates mounted one inch apart were placed in the exhaust stream. With no charge on the plates lead collection was 5 μg on one plate and 3.5 μg on the other. Plates were then charged by application of a potential difference of 1 kilovolt d.c. and run for the same time period. Collection on the positively charged plate was 7.3 μg and on the negatively charged plate 8.0 μg. The increase in lead collection by the positively charged plate was 2.3 μg or 46%, and by the negative plate 4.5 μg or 130%. The experiment was repeated with the apparatus modified as shown in Figure 21 to permit simultaneous determination of sample and blank. One set of plates is charged while the other set remains uncharged. The orientation of plates in the exhaust stream was changed so that each set saw identical exhaust conditions. The positive plates showed a collection efficiency with reference to the blank of 330% while the negative plate displayed a corresponding collection efficiency of 180%. The results suggest that a significant fraction of exhaust particles may bear an electrostatic charge. The possibility of induced charge effects by the field itself cannot be ruled out, however, and additional experiments are underway to resolve this matter.



Reproduced from best available copy.

Figure 21

G. Exhaust Filter

The filtration apparatus shown in Figure 22 has been constructed for collection of automotive exhaust particulates. Particles are collected on the microscope slides, and identification is by means of x-ray diffraction. The apparatus is shown assembled in the exhaust train in Figure 23.

H. Low-Lead Water

An all-quartz two-stage Hereaus still has been installed for preparation of low-lead water. Water distilled normally contains 0.02 to 0.05 μg Pb/ml. Tests have been made on the lead content of fresh distillate from the Hereaus apparatus and on the lead content after storage in high-density polyethylene. Water freshly distilled in the quartz apparatus contains 2.4 to 6.3 x 10^{-4} μg Pb/ml. Storage in high-density polyethylene containers does not appreciably enhance the lead content for periods up to 21 days.

I. Particle Size Distribution

We have deferred attempts to determine particle size distribution of atmospheric lead on the basis of the previously available 1 μg detection limit and the lack of high-volume cascade impactors. Recently made available analytical capabilities for determining lead to the nanogram level indicate that particle size distribution may be measured by means of a low volume (28 liter/min) cascade impactor. Flow rate considerations have ruled out the use of the Goetz size spectrometer.

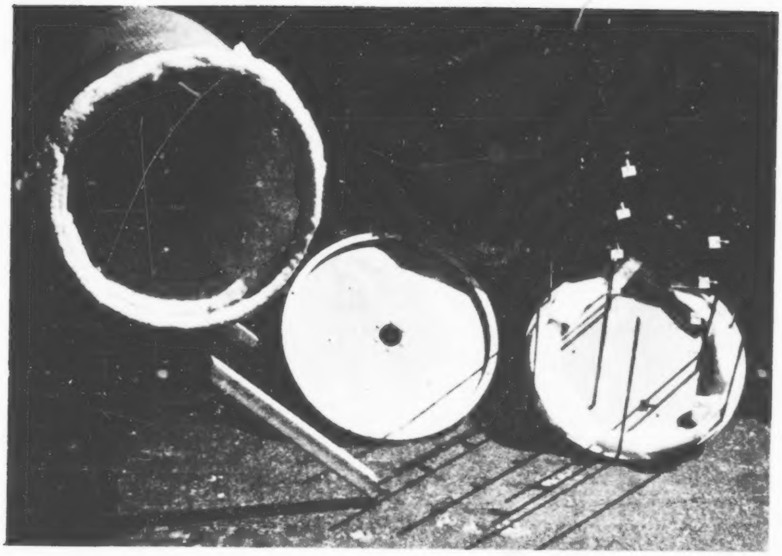


Figure 22

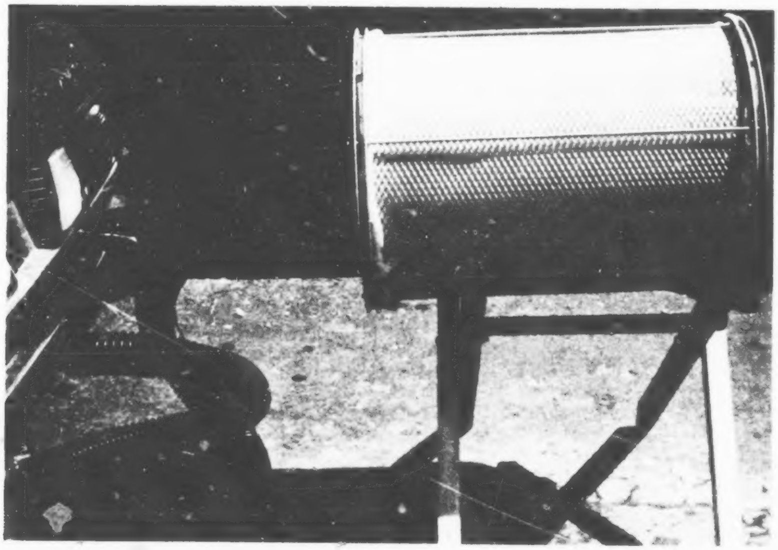


Figure 23

VI. INADVERTENT WEATHER MODIFICATION

A. Introduction

Effects of air pollution on weather are of considerable concern (SCEP group, 1970). The atmosphere plays a key role in maintaining the energy balance of the earth. Activities of man which change the composition of the atmosphere could change the energy balance and hence the mean terrestrial temperature. While the impact that a single man-made event could have on total atmospheric mass and energy fluxes is undoubtedly small, evidence for gradual changes in atmospheric composition is accumulating. The effects on global climate of such gradual compositional changes are therefore of some concern. Furthermore, temporary major elevations in pollutant concentrations can have pronounced localized effects such as in the case of the La Porte anomaly.

Constituents of traffic exhaust which can act as ice nuclei are of interest in the present investigation. Ice nucleating properties of automotive exhaust have received some study in recent years (Schaefer, 1966, 1968, 1969, 1970; Morgan, 1967, 1968; Landsberg, 1970; LaBreque, 1971). While fresh automobile exhaust does not supply large numbers of ice nuclei effective at warmer cloud temperatures, treatment of automobile exhaust with iodine significantly increases the number of ice nuclei. A proposed explanation is that lead contained in exhaust reacts with iodine to form PbI_2, an effective ice nucleant (Mason, 1962). Atmospheric iodine levels of several nanograms per cubic meter have been reported (Lininger _et al_., 1966). We have undertaken an investigation of the role of automotive lead in inadvertent weather modification.

B. Nucleation Activity of Leaded and Unleaded Exhaust

Ice nucleation tests on various engine exhausts were carried out in 10-liter mixing and expansion chambers and in the CSU isothermal cloud chamber. The isothermal chamber shown in Figure 24 is essentially a 2 m^3 chamber maintained at a constant temperature within 1°C. Constant input of supercooled water droplets is provided. Ice crystals formed are collected on microscope slides at the bottom of the chamber, and the total number is determined microscopically. Multiplication of this number by the ratio of the total bottom area to the slide area gives the total number of ice crystals produced. In the absence of iodination samples were collected in a 2-liter syringe and injected into the chamber without further dilution. In iodination experiments, 0.2 liter of iodine-saturated air was introduced into the syringe, and the remaining syringe volume was filled with exhaust. In terms of a reasonable estimate of the lead content of exhaust from combustion of regular gasoline, the stoichiometric ratio of iodine to lead was about 1000. Numerical results of the experiments are given in Table XII. A histogram of the data is shown in Figure 25.

Test results show that ice crystal production per liter of untreated exhaust is essentially identical for leaded and lead-free fuel. In the iodination experiments, the number of ice crystals produced was in general much greater than that produced by pure exhaust. Again, there is little difference between leaded and nonleaded gasoline. It must be concluded that if automotive lead acts as an ice nucleant or if lead iodide produced by the reaction between lead-containing exhaust and iodine vapor acts as an ice nucleant, this effect is minor compared

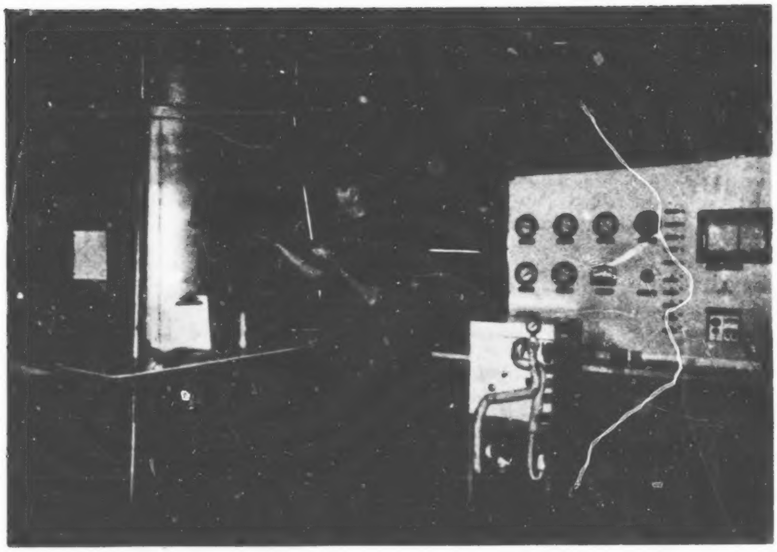


Figure 24

Reproduced from best available copy.

TABLE XII

Table of Measurements of Numbers of Ice-Producing Nuclei Per Liter in Leaded and Unleaded Gasoline Exhaust With and Without Treatment With Iodine Vapor

(Temperature = - 22.2 ± 1.3°C)
(Minimum Detectable Count = 2.53×10^5)

	Sample	Number	Range	Average	Deviation	Probable Error
without iodine vapor	Background	13	$0-1.52 \times 10^5$	4.56×10^4	5.34×10^4	3.60×10^4
	Room Air	9	$0-1.52 \times 10^5$	3.37×10^4	4.33×10^4	2.91×10^4
	Outside Air	3	$0-2.53 \times 10^5$	7.60×10^4	6.99×10^4	4.71×10^4
	Propane	5	$5.07 \times 10^4-3.55 \times 10^5$	2.02×10^5	1.52×10^5	1.01×10^5
	Regular Gasoline	5	$5.07 \times 10^4-6.94 \times 10^6$	2.36×10^6	2.79×10^6	1.87×10^6
	Premium Gasoline	2	$1.01 \times 10^5-2.03 \times 10^5$	1.52×10^5	--	--
	Amoco Pb-free Gasoline	6	$0-1.52 \times 10^5$	8.36×10^4	4.33×10^4	2.91×10^4
	Amoco Pb-free Gasoline (2 cylinder enginer)	3	$5.07 \times 10^4-1.01 \times 10^5$	6.84×10^4	1.77×10^4	1.27×10^4
with iodine vapor	Room Air	6	$5.63 \times 10^4-2.42 \times 10^6$	7.26×10^4	1.15×10^6	7.77×10^5
	Outside Air	7	$2.25 \times 10^5-5.97 \times 10^6$	2.98×10^6	2.22×10^6	1.50×10^6
	Propane	6	$3.38 \times 10^5-2.98 \times 10^6$	1.38×10^6	8.40×10^5	5.63×10^5
	Regular Gasoline	7	$8.48 \times 10^7-3.36 \times 10^8$	2.17×10^8	1.02×10^8	6.87×10^7
	Premium Gasoline	2	$1.74 \times 10^8-2.06 \times 10^8$	1.90×10^8	--	--
	Amoco Pb-free Gasoline	8	$5.91 \times 10^7-1.16 \times 10^9$	3.81×10^8	4.11×10^8	2.75×10^8
	Amoco Pb-free Gasoline (2 cylinder engine)	4	$1.29 \times 10^7-7.84 \times 10^7$	3.44×10^7	2.34×10^7	1.58×10^7

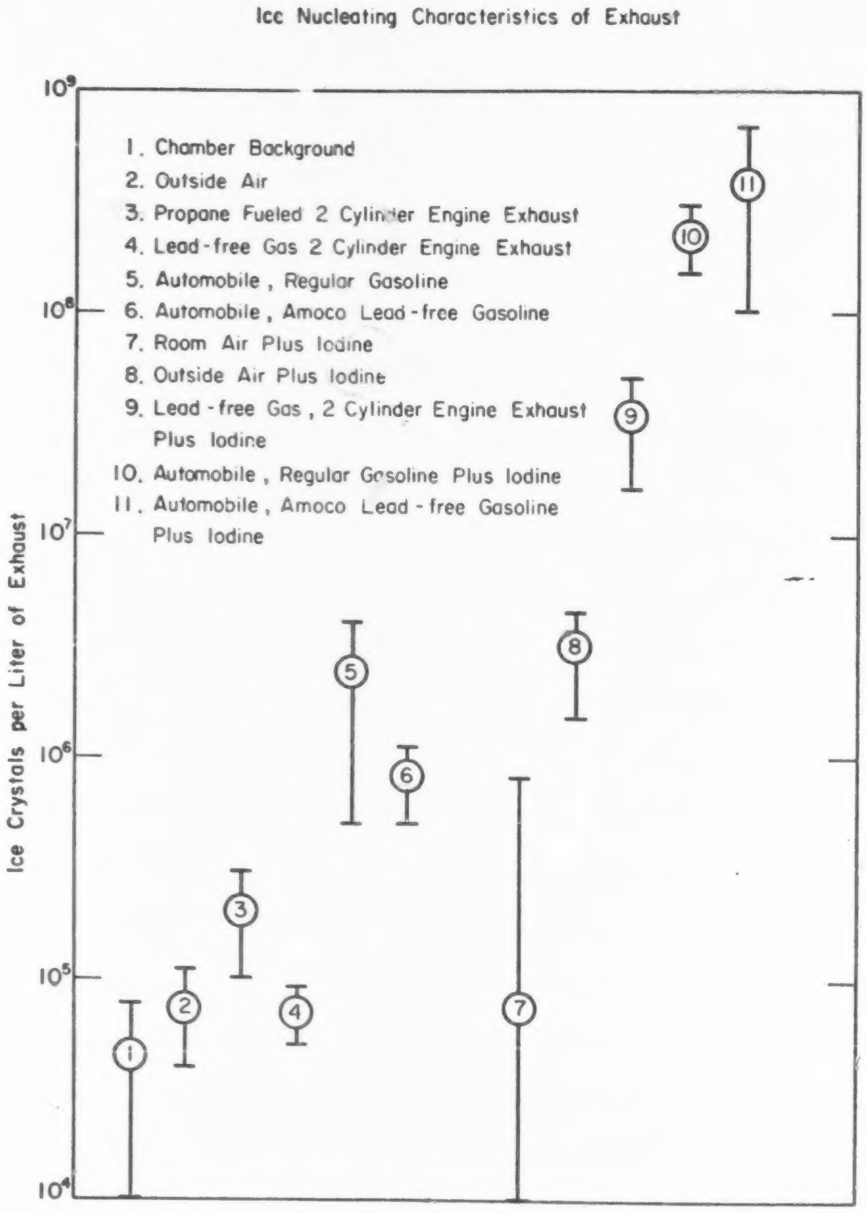

Ice Nucleating Characteristics of Exhaust
Ice Crystals per Liter of Exhaust
10^9
10^8
10^7
10^6
10^5
10^4
1. Chamber Background
2. Outside Air
3. Propane Fueled 2 Cylinder Engine Exhaust
4. Lead-free Gas 2 Cylinder Engine Exhaust
5. Automobile, Regular Gasoline
6. Automobile, Amoco Lead-free Gasoline
7. Room Air Plus Iodine
8. Outside Air Plus Iodine
9. Lead-free Gas, 2 Cylinder Engine Exhaust Plus Iodine
10. Automobile, Regular Gasoline Plus Iodine
11. Automobile, Amoco Lead-free Gasoline Plus Iodine
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪

Figure 25

to ice nucleating properties of other exhaust components both in the presence and absence of iodine. It thus seems unlikely that conversion to lead-free fuels will reduce the potential of traffic exhaust for inadvertent weather modification.

C. Background Nucleation Activity at Climax, Colorado

Background nucleation activity has been monitored over a 17-year period at Climax, Colorado, elevation 11,300 feet (Grant, 1971). Since this elevation corresponds closely to cloud formation levels, test results can be related to cloud processes occurring under field conditions. While the Climax location is relatively far removed from major urban areas, atmospheric diffusion processes would normally be expected to provide the mixing necessary for long range transport of urban pollution. It is pointed out that consumption of leaded gasoline has increased steadily over the 17-year period from 1954 to 1971 (Lutz et al., 1970). The objective was therefore to learn if steadily increasing pollution from automobile traffic has altered the background (natural) nucleation activity at this location.

Plotted in Figure 26 are average annual ice nuclei concentrations (-20°C) by year. These data summarize approximately 16,000 observations made on unseeded days. High values observed for 1955, 1962, 1963, and 1966 are probably attributable to nearby cloud seeding activities and residual effects from seeded days. It is concluded that there is no persistent trend in average background ice nuclei concentration (-20°C) during this long period. It must be emphasized that the values plotted in Figure 26 are for activation at -20°C and there-

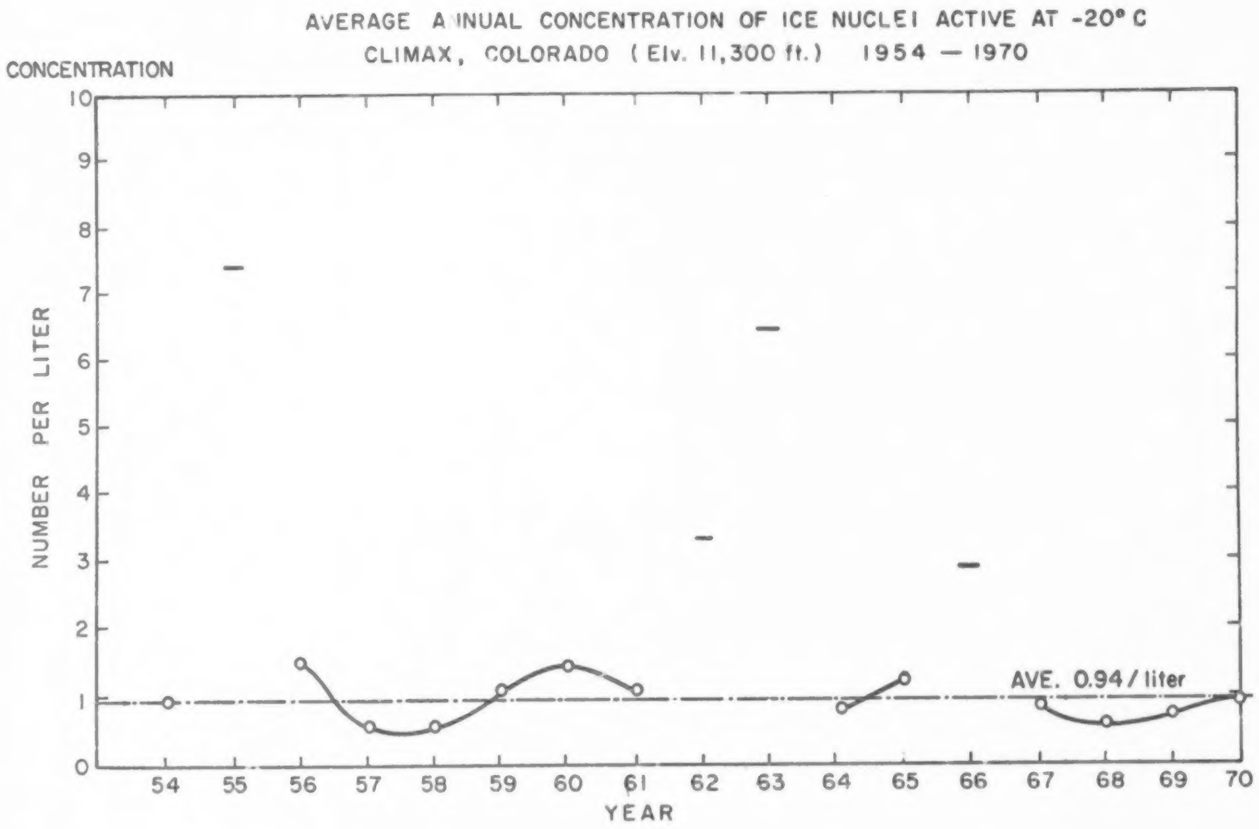

AVERAGE ANNUAL CONCENTRATION OF ICE NUCLEI ACTIVE AT -20° C
CLIMAX, COLORADO (Elv. 11,300 ft.) 1954 — 1970
CONCENTRATION
NUMBER PER LITER
0
1
2
3
4
5
6
7
8
9
10
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
YEAR
AVE. 0.94 / liter

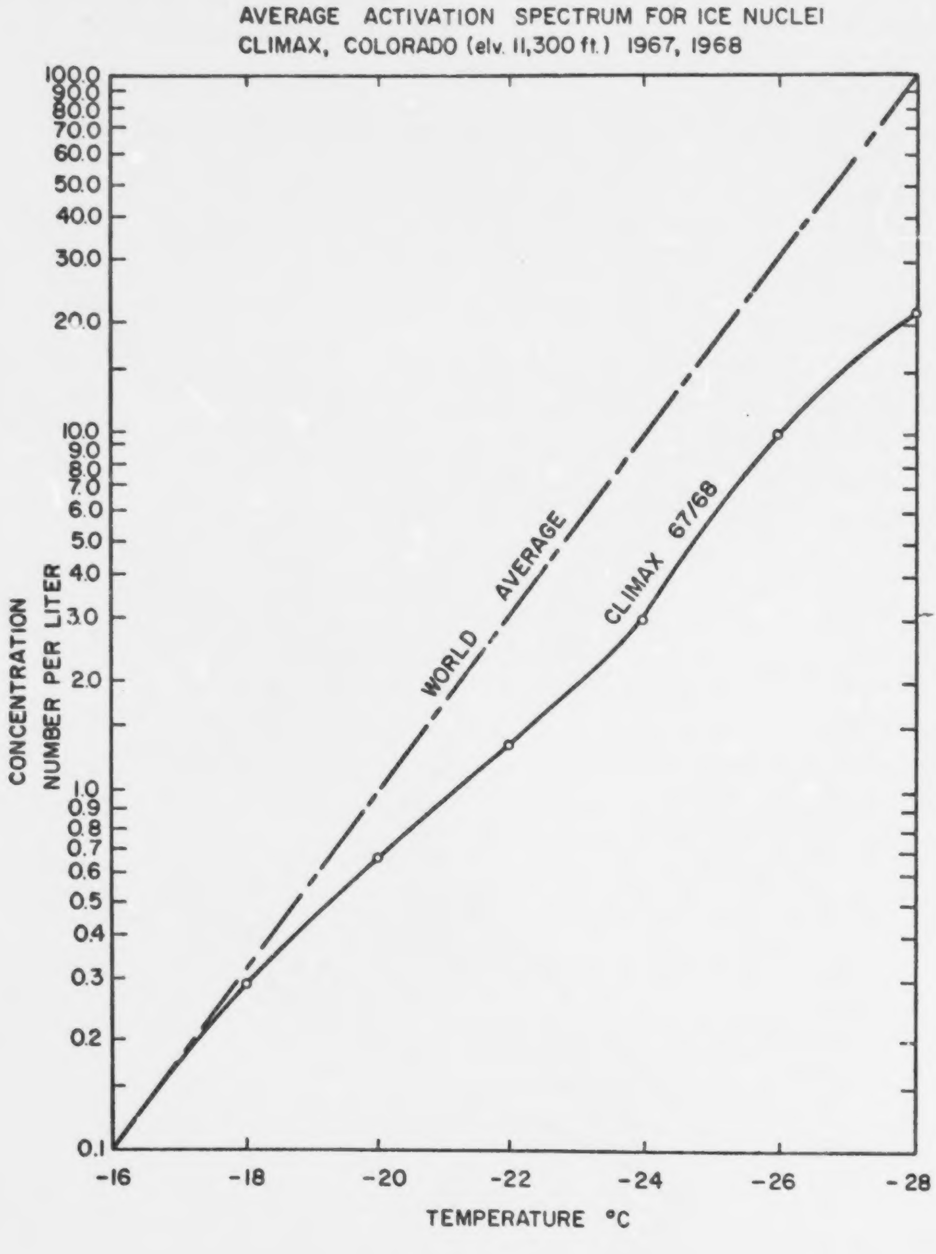
Figure 26

fore do not allow us to draw conclusions about nucleation activity of pollutants at other temperatures.

Activation spectra for background (natural) ice nuclei were measured. Shown in Figure 27 is the temperature activation spectrum for background nuclei measured at Climax during the period 1967-1968. These data represent averages of approximately 500 observations. The generally accepted worldwide activation spectrum for natural ice nuclei is also shown for reference. Down to between -18 and -20°C, the Climax values are in good agreement with background ice nucleation activity measured in other places around the world. At cooler temperatures, the Climax measurements are significantly lower than world average values. This is believed to be related to lower levels of atmospheric pollutants at the mountain site than at other, and generally more urban, observation sites.

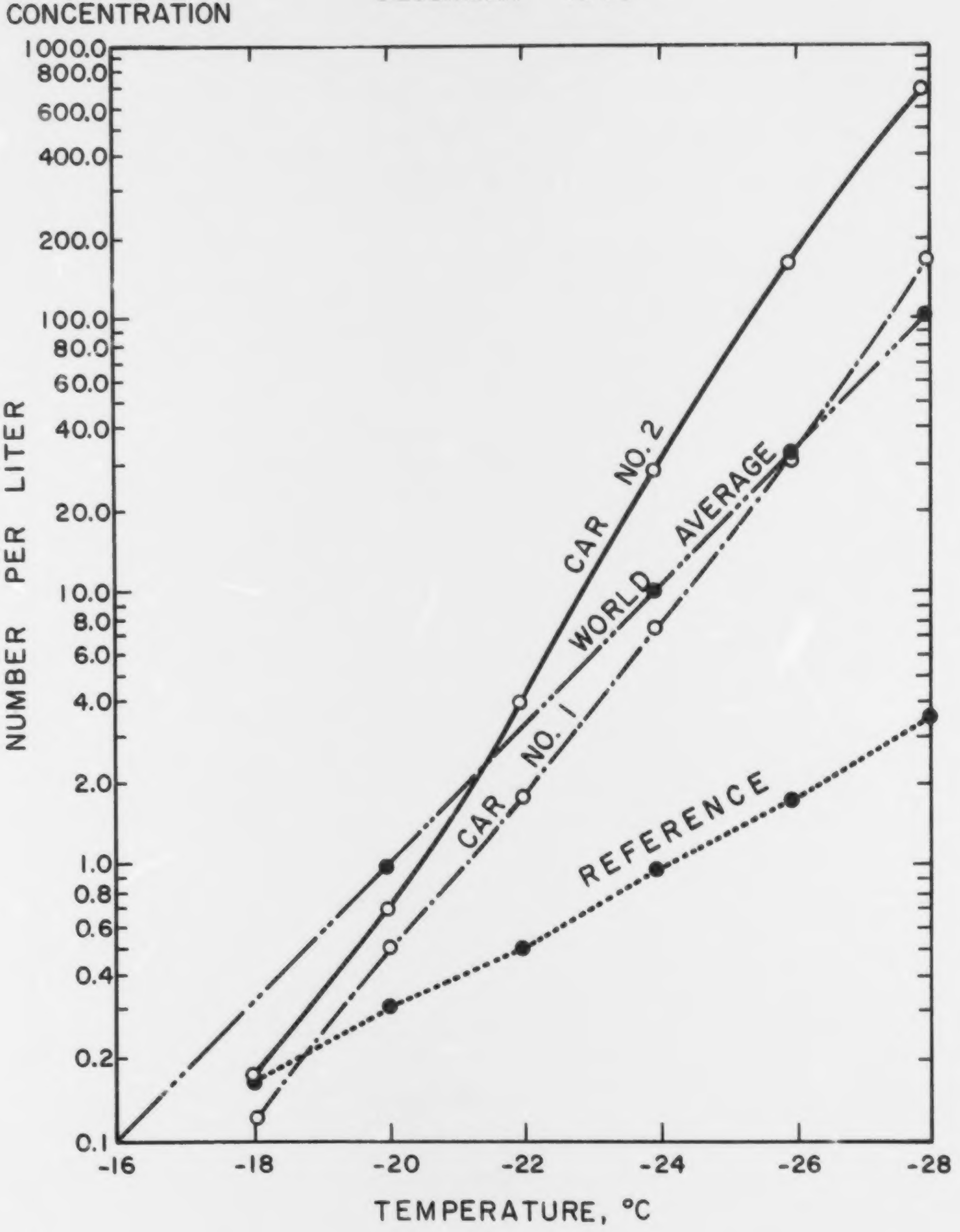
D. Activation Spectra for Automotive Exhaust

Figure 28 summarizes some results of pilot activation spectra tests on automobile exhaust. A baseline activation spectrum was established using an outside source of air. Exhausts were diluted with air in 2 m^3 polyethylene bags and then fed into the ice nuclei counter. The slope of the reference spectrum is similar to the slope obtained for background nuclei at Climax. The spectrum for Car #1 represents the average of five different tests. The spectrum for Car #2 represents the average of three individual test results. Test results at -18°C are indistinguishable within experimental error for the two automobile exhaust samples and the reference sample. However, as the tem-



AVERAGE ACTIVATION SPECTRUM FOR ICE NUCLEI
CLIMAX, COLORADO (elv. 11,300 ft.) 1967, 1968

Figure 27



ICE NUCLEI ACTIVATION SPECTRA FOR AUTO EXHAUST FROM TWO CARS. FORT COLLINS, COLORADO.
DECEMBER 1970

Figure 28

perature is lowered the reference and exhaust curves diverge. At lower temperatures, activation curves for automotive exhaust are similar to the worldwide activation spectrum. At -28°C the nucleation activity for automobile exhaust is greater than the reference activity by a factor of 10 to 100. Differences between spectra of the two automobile exhausts may reflect differences in engine performance. These data indicate that auto exhaust can serve as a source of effective ice nuclei at colder temperatures. The data also indicate that ice nucleation activity measured at -20°C would not reveal increases in ice nuclei due to increases in pollution levels since -18° to -20°C appears to be a reasonable threshold temperature range for auto emissions.

These cloud chamber tests indicate that while unaltered automobile exhausts can produce large numbers of ice nuclei at cooler temperatures, nucleation activity of automobile exhaust is indistinguishable from background at temperatures warmer than about -18°C. This is the temperature region for which an increase in precipitation from inadvertent seeding should occur. Since natural nuclei occur in sufficient numbers at temperatures of about -24°C and colder, the net effect of an increase in ice nuclei at these colder temperatures would be overseeding which could result in a precipitation decrease.

E. Continuing Work

Laboratory nucleation tests are planned to obtain temperature effectiveness spectra for automobile exhaust both in the presence and absence of iodine. Similar experiments are planned to investigate the effect of iodine vapor on atmospheric particulates under field conditions at Climax, Colorado. Techniques necessary to obtain an ice nuclei concentration profile along I-25 are under study. Increasing emphasis will be placed on field measurements to detect inadvertent weather modification phenomena occurring in the atmosphere. Laboratory tests will be relied upon to describe such phenomena and to obtain a physical link with atmospheric composition. While the present study emphasizes the role of lead in inadvertent weather modification, our tests indicate that other exhaust components should also be studied. It is thus planned to broaden the scope of the present study to include other atmospheric constituents, especially those contained in automobile exhaust. It is hoped that extension of the present study will enable us to evaluate effects of nucleation temperature, aging, and exposure to various atmospheric constituents.

VII. BIOACCUMULATION OF LEAD

A. Introduction

The physiological effects of lead on living systems are of major importance in assessing the impact of lead pollution from traffic exhaust on man. There is considerable disagreement concerning the contribution of lead from traffic exhaust to lead intoxication in humans. While atmospheric lead levels have increased markedly in certain urban communities, blood lead levels in residents have remained nearly constant (Golz, 1971). However, elevated blood lead levels have been reported for persons living in high traffic density areas (Thomas, 1967; Goldsmith, 1969). The question of whether lead pollution from traffic exhaust poses a health hazard for humans is thus by no means settled. The present level of understanding of the history of lead in a biological system is decidedly inadequate.

Experiments have been initiated to monitor biological effects of lead pollution from Interstate Highway 25 traffic. The ubiquitous Peromyscus maniculatus (deer mouse) has been selected as a biological integrator. This species lives about two years in the natural state and is found in sufficient numbers both very close to the highway and in remote regions relatively free of lead pollution from traffic exhaust. The purpose of the experiments is to determine whether the mice accumulate lead and whether the accumulation is organ-specific under environmental conditions. Furthermore, we wish to determine the major pathway for lead accumulation.

B. Lead Uptake in Mice

Two groups of adult deer mice, Peromyscus maniculatus, have been collected from two areas in Colorado and analyzed for total body burden. The specimens designated "Craig" were obtained from a rural area near Craig, Colorado during the period November 16-18, 1970. Trap sites were far removed from any roadway or highway with high traffic volume. The specimens designated "I-25" were trapped adjacent to Interstate Highway 25 between Fort Collins and Denver during the period September 30-October 31, 1970. Traps were placed in grassy areas between the edge of the pavement and the fence boundary along the highway. The width of these areas varied from approximately 60-85 feet, and traps were placed on the average about 88 feet from the center of the highway. Upon removal from the trap an animal is placed in a plastic bag which is then sealed. After return to the laboratory the sealed containers are placed in a freezer. Prior to preparation for chemical analysis the animal is removed from the plastic bag and placed in a container with cyanogas to kill any disease-bearing parasites that might be present. An animal is then thoroughly washed by hand with distilled water to remove dust and debris from the fur. Plastic gloves are worn during washing. Chemical analysis is by atomic absorption spectrometry.

The analytical results are given in Table XIII. The mean total lead body burdens are 1.41 μg/g dry wt. for Craig mice and 4.90 μg/g dry wt. for Interstate 25 mice. Standard deviations are 1.79 and 4.29 μg/g dry wt., respectively. Each group consists of 20 samples. Application of the student t test indicates that the difference is significant at the 99.5% confidence level. The difference may be attributable

TABLE XIII

TOTAL LEAD BODY BURDEN IN DEER MICE (*Peromyscus maniculatus*)

	Craig	I-25
No. of Specimens	20	20
Mean, μg Pb/g dry weight	1.41	4.90
Range, μg Pb/g dry weight	7.70	15.20
Std. Dev., μg Pb/g dry weight	1.79	4.29
t	3.36	
p	0.005	

to a difference in tissue lead concentration but may also be attributable to greater lead concentration in the stomach contents of mice from the I-25 group. Further, more detailed analysis involving individual organs of individual animals is expected to substantiate one of the proposed explanations.

Considerable effort has been devoted to development of surgical techniques for excising specific organs without contamination. We have found that rubber gloves worn during earlier dissection contained talcum powder having a high lead content. We also found that the laboratory in which the first dissections were carried out was at one time painted with lead-containing paint. Significant lead levels were found in dust collected from the laboratory walls, table surfaces, and instruments. Rather elaborate precautions are now taken to prevent contamination during dissection.

C. Autopsy Data

Other experimental activities designed to shed light on bioaccumulation of lead are those involving analysis of tissues from chinchillas and humans. Arrangements are underway to obtain bone, skeletal muscle, and blood for all Larimer County coroner cases. C. G. Wilber is deputy coroner for Larimer County. These materials will be analyzed to detect correlations with age, sex, occupation, cause and manner of death, and residence.

D. Microbial Systems

Experiments have been initiated to investigate the interaction between lead and bacteria commonly found in soil and ground water systems. Pilot experiments which were designed to detect gross effects indicate that if lipid-soluble organic lead compounds are formed by microbiotic processes in the soil and water systems thus far examined, the quantities are quite small compared to the amounts of inorganic lead present. The pilot experiments also indicate that the lead levels thus far investigated do not appreciably inhibit bacteriological growth rates.

VIII. LEAD IN SOIL AND PLANTS

A. Introduction

Much of the lead entering the environment through combustion of leaded gasoline is deposited at the soil/atmosphere interface. Approximately half of the particulate lead exhausted over the lifetime of a vehicle is of sufficient size to be deposited by gravitational settling very close to a roadway. Precipitation scavenging processes are probably more important for removal of smaller particles which have negligible gravitational settling velocities. While smaller particles are thereby ultimately removed to the soil/atmosphere interface, atmospheric dilution is such that the lead content of rainfall only occasionally exceeds the accepted maximum concentration for lead in drinking water (Lazrus *et al.*, 1970). It therefore seems reasonable to expect that any gross soil effects associated with automotive lead would be confined to a relatively narrow zone close to the highway. Further away, the contribution of automotive lead to the lead content of soil would be small since the world average natural lead concentration in soil uncontaminated by traffic exhaust is about 16 ppm. Soil near the roadbed at Colorado sampling sites studied averages 22.9 ppm lead. Ordinary chemical analysis for total lead does not distinguish between natural and automotive lead. However, it may be possible to distinguish between natural and automotive lead by means of an isotope ratio technique (Ault, 1970).

Laboratory and field experiments were undertaken to learn the transport and accumulation characteristics of automotive lead in soil. The objective of the field studies is to experimentally determine the accumulation pattern of automotive lead in soil near the highway sampling sites. These experiments are an integral part of the broader project objective to develop a systems approach for studying environmental transport of trace constituents. We are also very much concerned with the time scale for transport and immobilization of lead in soil. Laboratory studies were undertaken to simulate certain processes which are believed to occur under environmental conditions. While results of laboratory experiments may not always be applicable under field conditions, they offer the advantage of studying selected processes under carefully controlled conditions and are therefore helpful in understanding phenomena encountered in the environment.

B. Site Selection

Factors governing site selection were discussed earlier in the section dealing with atmospheric transport. Two additional points appropriate for mention here deal with soil composition. First, it is pointed out that soil samples obtained very close to the roadway are of quite different composition than soil samples obtained a few feet away from the roadway. Very close to the roadway, material collected consists largely of gravel and tar. This type of material posed special problems during subsequent chemical analysis. The second point is that soil very near a roadway should not be regarded as natural soil since this material was undoubtedly disturbed during highway construction. Soil used for filler very near a roadway may have been imported from other locations. While it is recognized that these physical factors could affect soil background levels and accumulation characteristics, it is emphasized that the soil experiments undertaken were designed to detect trends and gross effects. Moreover, it was established experimentally that soil composition is relatively uniform in the general area of proposed sampling sites.

C. Field Measurements

1. Background Lead in Soil

The baseline value of lead in soil typical of the field site locations has been determined from the large number of samples and is 22.9 ppm with a standard deviation of 4.4 ppm. This value is somewhat higher than the world average of 16 ppm and may be traceable to geologic origin. We are collecting a fairly large number of soil samples from various areas in the State of Colorado. These areas include high exposure regions and very remote regions. Also, soil samples have been obtained from areas where past and present lead mining activity has been or is significant. When completed, survey measurements should give a good picture of the natural lead levels in the soil as well as the current levels near the major sources of traffic exhaust.

2. Lead in Roadside Soil

The lead content of soil was measured both as a function of distance from the highway and depth. Analysis of 0-6 inch samples at the 144th Avenue overpass on Interstate Highway 25 reveals that lead concentrations are highest immediately adjacent to the roadway. As shown in Figure 29, soil lead concentration rapidly diminishes with both

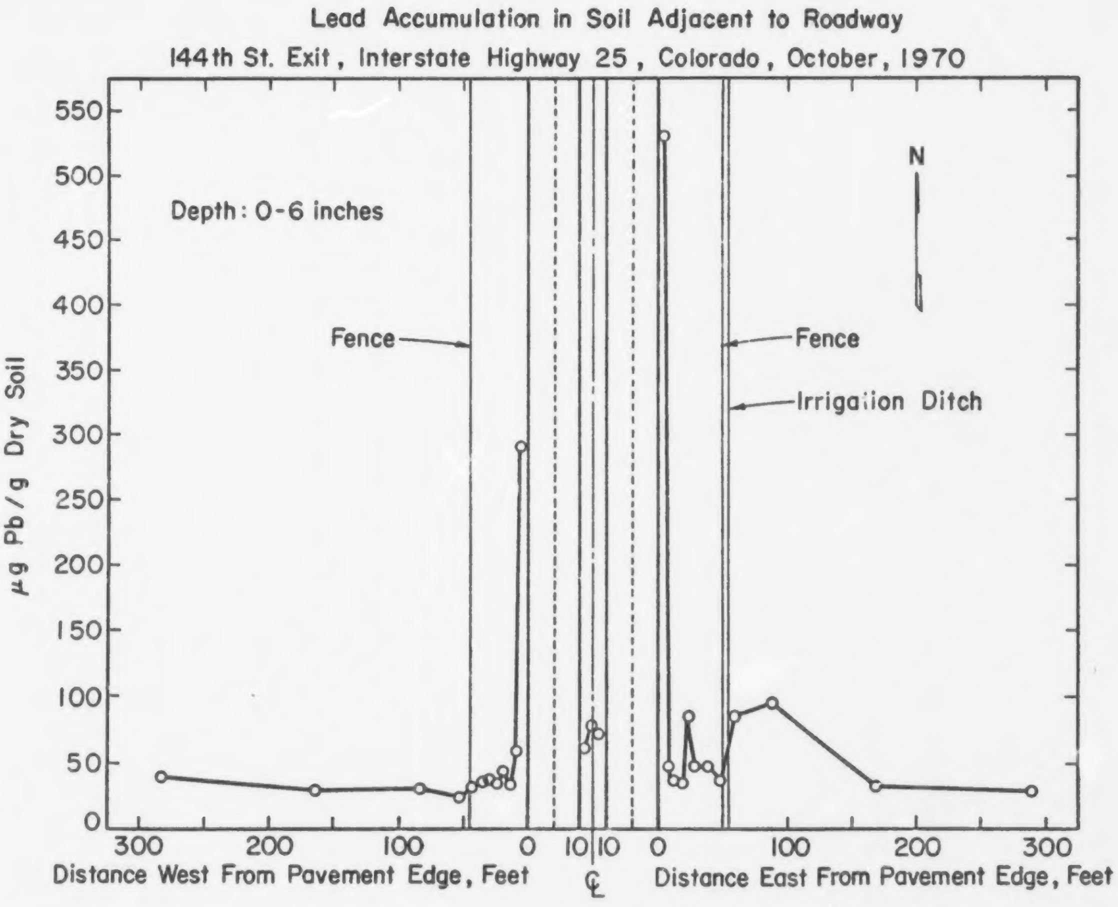
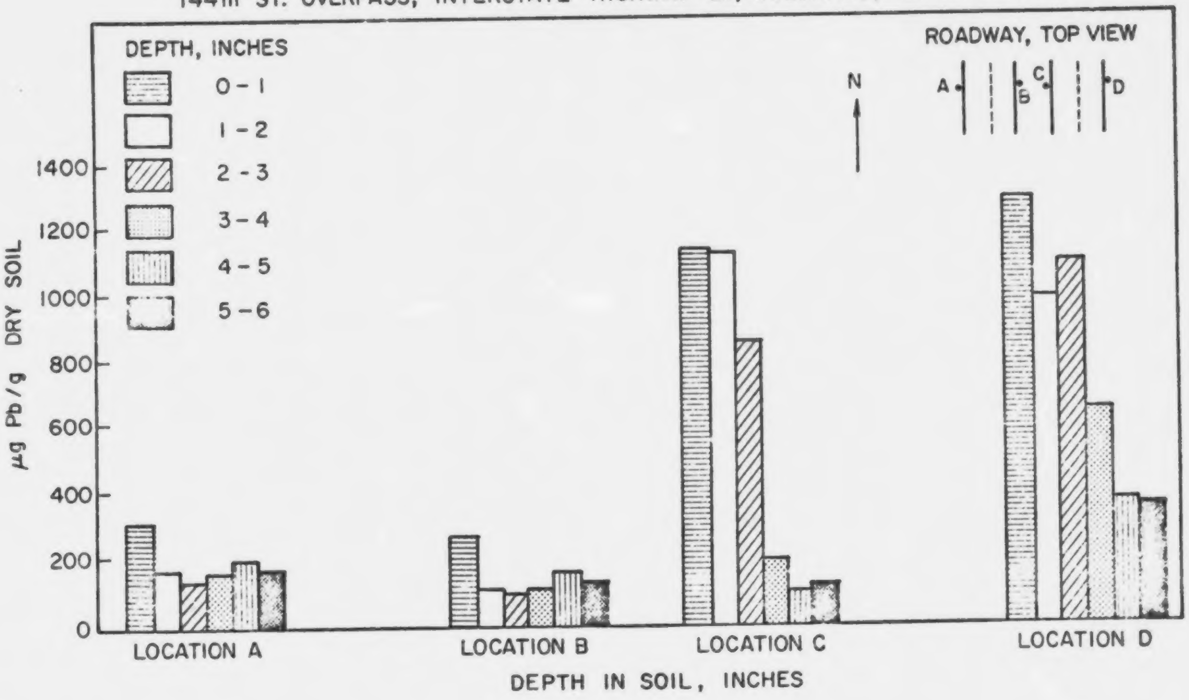

Lead Accumulation in Soil Adjacent to Roadway
144th St. Exit, Interstate Highway 25, Colorado, October, 1970
Depth: 0-6 inches
N
Fence
Fence
Irrigaiion Ditch
µg Pb / g Dry Soil
550
500
450
400
350
300
250
200
150
100
50
0
300
200
100
0
10
10
0
100
200
300
Distance West From Pavement Edge, Feet
℄
Distance East From Pavement Edge, Feet

Figure 29

depth and distance from the highway. Measured lead values for soil samples obtained further than about 100 feet from the highway are essentially indistinguishable from background. Lead values reach about 530 ppm on the east side of the northbound lane and nearly 370 ppm on the west side of the southbound lane. Prevailing winds are generally either northerly or southerly. Average traffic flow rates for the two lanes are essentially identical.

Preferential buildup of lead in soil immediately adjacent to the northbound lane was confirmed by depthwise analysis of soil samples obtained very near the roadway surface. These results are presented in Figure 30. While it must be emphasized that the composition of material obtained immediately adjacent to the roadway is not typical of soil, it seems clear that the lead content of this material decreases with increasing depth. This material is also atypical in that lead levels are significantly higher than background for the 5-6 inch samples. The mechanism by which preferential buildup occurs may involve reinjection of lead particles deposited on the west side of the highway with subsequent redeposition on the east side of the highway. It is known that westerly Chinook winds are fairly common during certain periods of the year. Experiments are also underway to correlate observed lead accumulation patterns with highway slope since it is known that load conditions can affect lead emission rates (Habibi et al., 1970).

The soil data obtained thus far indicate that soil samples obtained at depths greater than six inches possess lead contents indistinguishable from background. Surface soil samples obtained more than 100 feet from the roadway must also be regarded as indistinguishable from background at



LEAD ACCUMULATION IN SOIL ADJACENT TO ROADWAY
144th ST. OVERPASS, INTERSTATE HIGHWAY 25, COLORADO, SEPTEMBER, 1970

Figure 30

the 95% confidence level. These data strongly suggest that larger lead particles with appreciable settling velocities do not travel far from the source. Moreover, deposited automotive lead does not appear to penetrate appreciably into the upper soil stratum. These experiments do not reveal the fraction of lead contained in gasoline which falls out close to the highway.

D. Radiotracer Experiments

The rate at which Pb-210 is depleted from solution has been investigated by means of radiotracer experiments. It is emphasized that the term immobilization is used because we cannot at this time distinguish among precipitation, adsorption, and absorption as immobilization mechanisms. Data for two different soils are shown in Figure 31. In this experiment, ten grams of soil is placed in contact with 70 ml of spiked Pb-210 solution. The initial activity of the solution was determined by evaporating two ml on a planchet and then counting in a proportional counter. Samples were subsequently withdrawn at various time intervals and the activity determined similarly. The tracer experiments indicate that for both soils examined, lead is rapidly immobilized with a limiting count rate being reached in approximately 24 hours. It is also seen in Figure 31 that the two soils differ widely in composition. The soil with the higher organic matter content may be more effective in removing Pb-210 from solution.

E. Rate of Immobilization

The rate at which lead is depleted from lead nitrate solution by

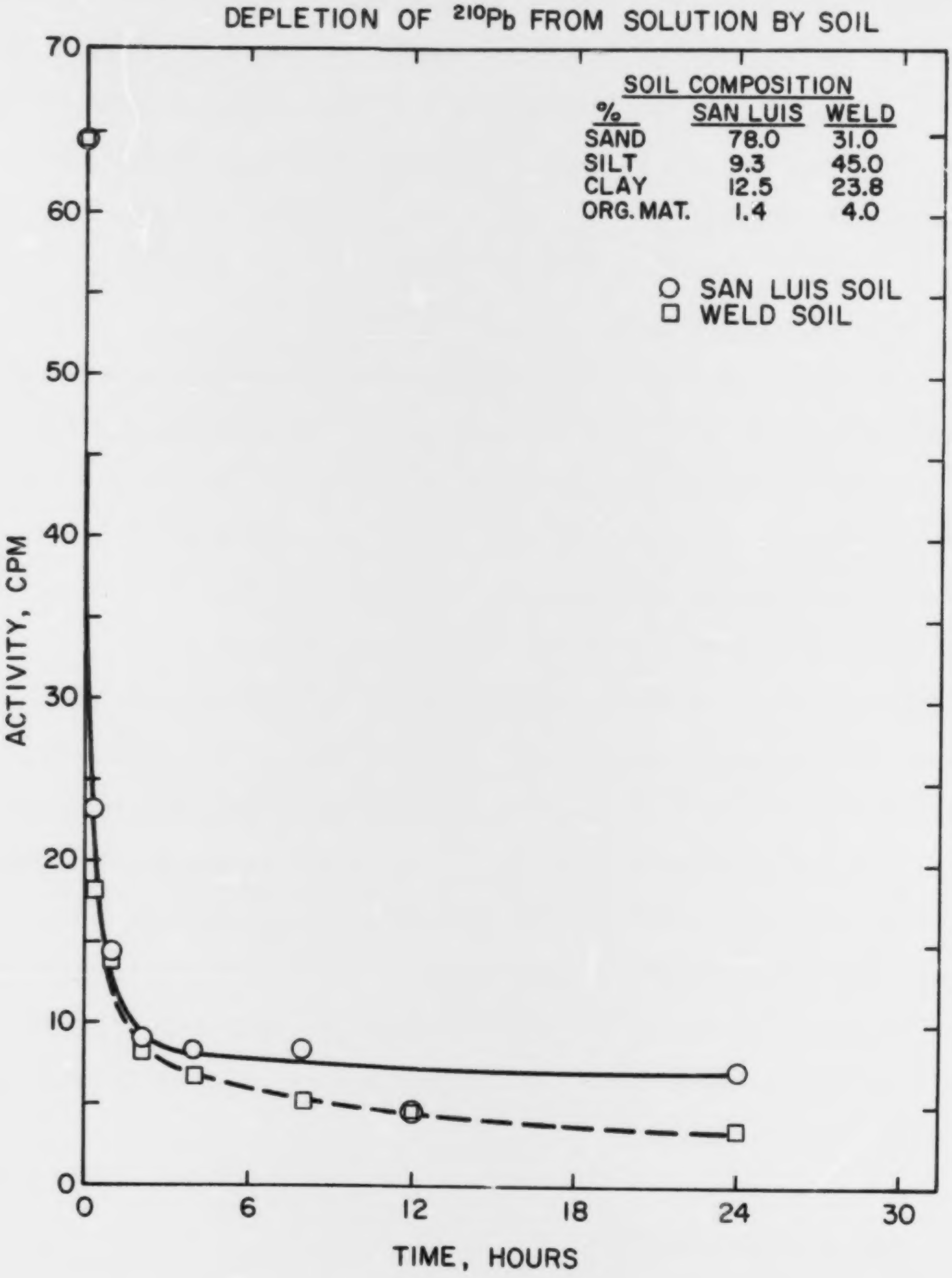

DEPLETION OF 210Pb FROM SOLUTION BY SOIL
SOIL COMPOSITION
% | SAN LUIS | WELD
SAND 78.0 31.0
SILT 9.3 45.0
CLAY 12.5 23.8
ORG. MAT. 1.4 4.0
○ SAN LUIS SOIL
□ WELD SOIL
ACTIVITY, CPM
TIME, HOURS
0
10
20
30
40
50
60
70
0
6
12
18
24
30

Figure 31

soil was measured for four soil types. A ten-gram sample of each soil type was placed in contact with 95 ml of lead nitrate solution at the initial concentration of approximately 900 ppm. Five ml of solution was periodically withdrawn and centrifuged for lead analysis by AAS. The results are plotted in Figures 32 and 33 as the amount of lead adsorbed as a function of time. It is again emphasized that the term immobilization might be more appropriate because of the multiplicity of processes by which soil could remove lead from solution. These experiments indicate that a limiting value is approached quite rapidly with little fractional change occurring after 24 hours. These results are consistent with the radiotracer experiment.

F. Equilibrium Immobilization Study

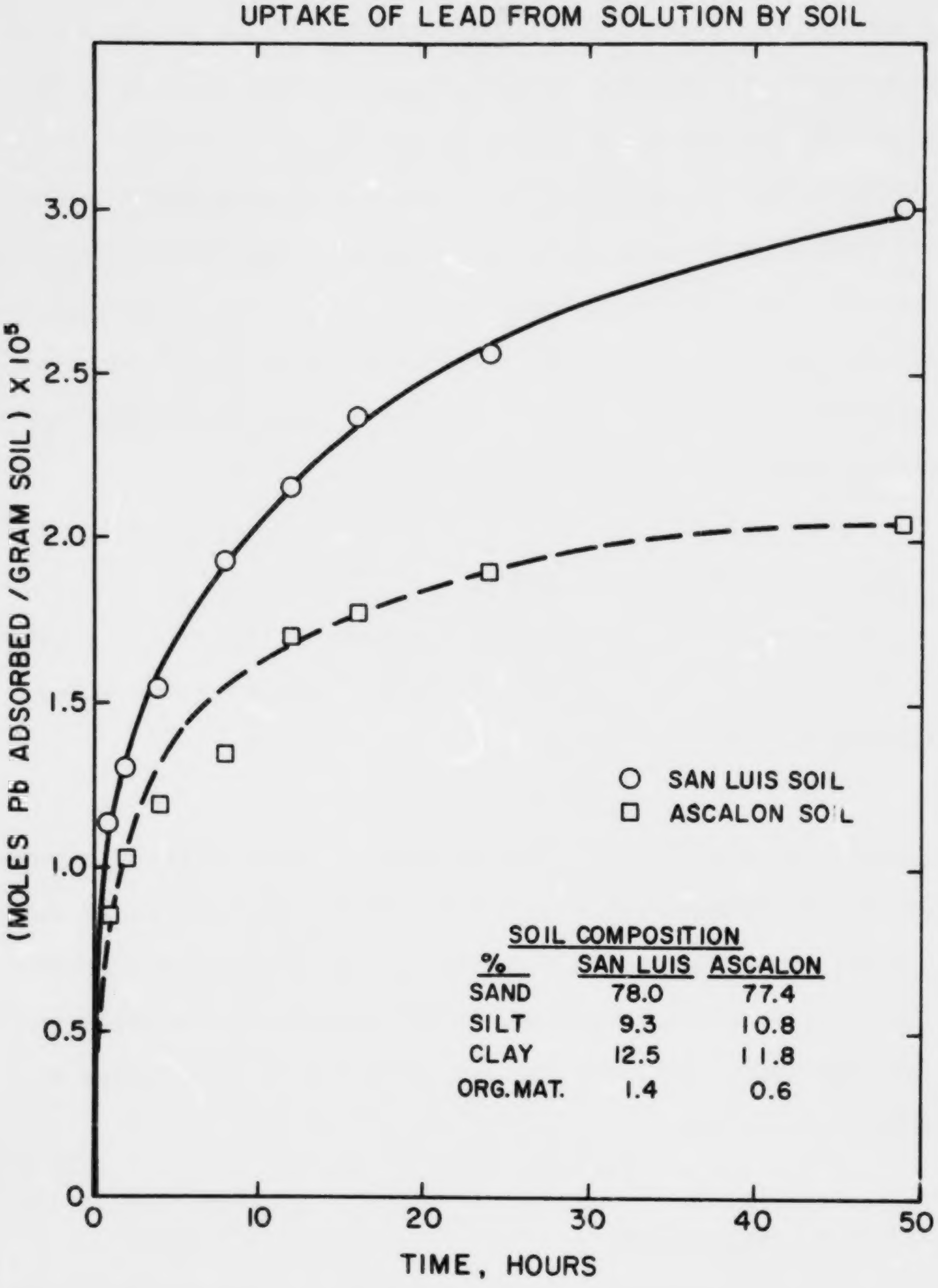
Figure 34 is a log-log plot of the data. A linear least squares fit of the data to the Freundlich sorption isotherm results in the following expression:

$$n_{ads} = 1.9 \times 10^{-4} C_{Pb}^{0.27}$$

This equation describes the observed sorptive behavior at 30° between equilibrium concentrations of 10^{-5}M and 10^{-1}M. It was expected that at higher concentrations the sorption would display Langmuir behavior in which a limiting sorptive capacity is approached. Continuing equilibrium experiments involve higher concentrations to detect onset of Langmuir-like behavior.

G. Column Leaching Studies

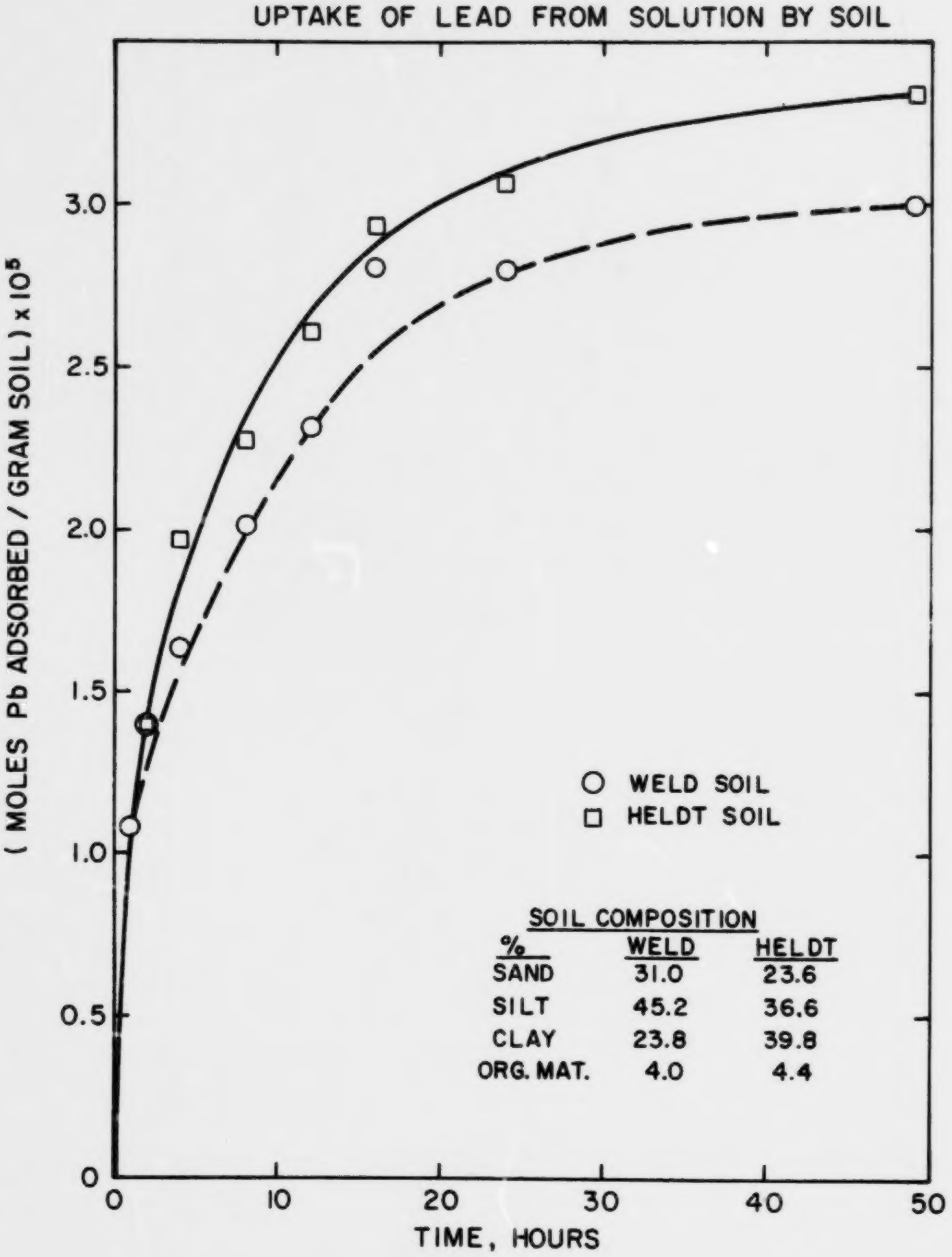
Several gross experiments were conducted to determine the relative



SOIL COMPOSITION

%	SAN LUIS	ASCALON
SAND	78.0	77.4
SILT	9.3	10.8
CLAY	12.5	11.8
ORG. MAT.	1.4	0.6

Figure 32



SOIL COMPOSITION

%	WELD	HELDT
SAND	31.0	23.6
SILT	45.2	36.6
CLAY	23.8	39.8
ORG. MAT.	4.0	4.4

Figure 33

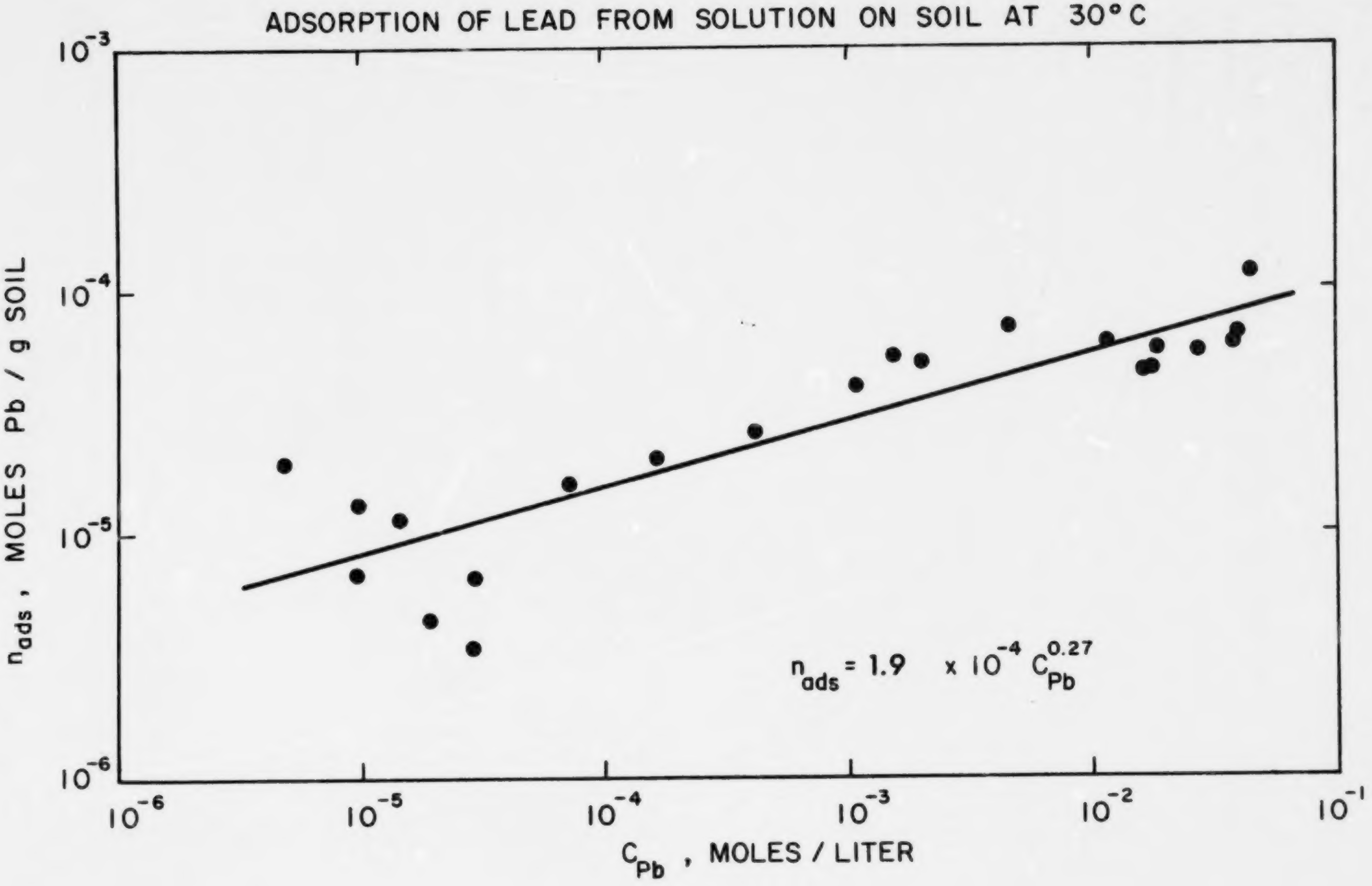

ADSORPTION OF LEAD FROM SOLUTION ON SOIL AT 30°C

Figure 34

ease with which immobilized lead could be removed from soil columns by leaching with distilled water. Four glass columns containing different soil samples were prepared using 2x25 cm glass tubing. Soil characteristics, column volume, and micrograms of lead added are given in Table XIV. Added lead was applied in a 10 ml volume of water. The quartz sand sample was intended to serve as a reference. The second 10 ml volume applied to the quartz sand-containing column was found to contain 198 µg, 7.8% of the original, and the third 10 ml volume contained 123 µg (4.8%). In the four soil samples three column volumes of water failed to remove more than 15 µg of lead in each case. Depthwise analysis of the four soil columns revealed that the added lead was found in the uppermost inch of the soil column. These results indicate that immobilized lead is only slowly removed by water leaching. The data for the quartz sand column are of interest in that leaching was not particularly rapid for this material in spite of its relatively low exchange capacity.

TABLE XIV

SOIL LEACHING STUDIES
SOILS, COLUMN VOLUME, AND MICROGRAMS OF LEAD ADDED

Soil	%				pH	Column volume (ml)	µg Lead Added in One Column Volume
	Sand	Silt	Clay	O.M.			
Quartz sand	100.0				--	29	2552
Ascalon	77.4	10.8	11.8	0.6	7.8	33	2904
San Luis	78.0	9.3	12.5	1.4	7.9	30	2640
Weld	31.0	45.2	23.8	4.0	6.5	35	3080
Heldt	23.6	36.6	39.8	4.4	6.5	25	2200

H. Surface Area, Cation Exchange Capacity

In addition to the gross compositional characterization such as those described above, some effort will be expended to obtain characteristic values for cation exchange capacity and surface area. These parameters are widely used in soil science and may be of value for more fully describing soils studied. However, it is not expected that these measurements will greatly affect the generalizations which have been developed from experiments reported herein.

I. Lead in Plants

Uptake of lead by crops grown in lead-contaminated air and soil has received considerable study (Ter Haar, 1970; Ter Haar, 1971; Motto et al., 1970; Dedolph et al., 1970). There seems to be general agreement that airborne lead from traffic exhaust does not significantly increase the lead content of the edible portion of most crops. Leafy portions of crops grown near busy highways might contain higher lead concentrations. However, even in the absence of airborne lead, leafy portions of these plants contain more lead than do other parts. There also appears to be general agreement that a severalfold increase of lead in soil does not measurably change the concentration of lead in plants.

The purpose of the present plant investigation is to learn the extent to which the above generalizations are applicable to naturally occurring plants and crops exposed to lead from traffic exhaust along I-25. Furthermore, plants may influence the transport and accumulation properties of the soil system. We are additionally interested in translocation of lead in the plant and the possible existence of specific sinks for lead in plants. The relative importance of foliar versus root uptake and the distinction between lead deposited or imbedded on foliar surfaces and lead absorbed within the leaf structure is of interest.

Pilot laboratory experiments with plants have been initiated. Primary emphasis has been upon developing experimental techniques by which plants can be exposed to airborne lead over extended period. A technique based on thermal volatilization of a metallic salt is being examined (Edwards, 1969).

Plants grown in lead-doped soil have been analyzed for lead. The plants were harvested as shoots 19 days after planting. Lead was added as lead nitrate. Lead uptake is shown as a function of the amount of lead added in Figure 35. The data indicate that lead uptake increases very slowly with added lead. With the exception of sugar beet shoots, the results are quite similar. For sugar beets the lead accumulation is higher by a factor of approximately four at all concentrations. This crop is of special interest in the State of Colorado and is oftentimes found growing nearby a highway. It should be emphasized that the lead concentrations were considerably higher than those that might be encountered in soil near even a very heavily traveled highway. Additional experiments are planned to explore the significance of these findings.

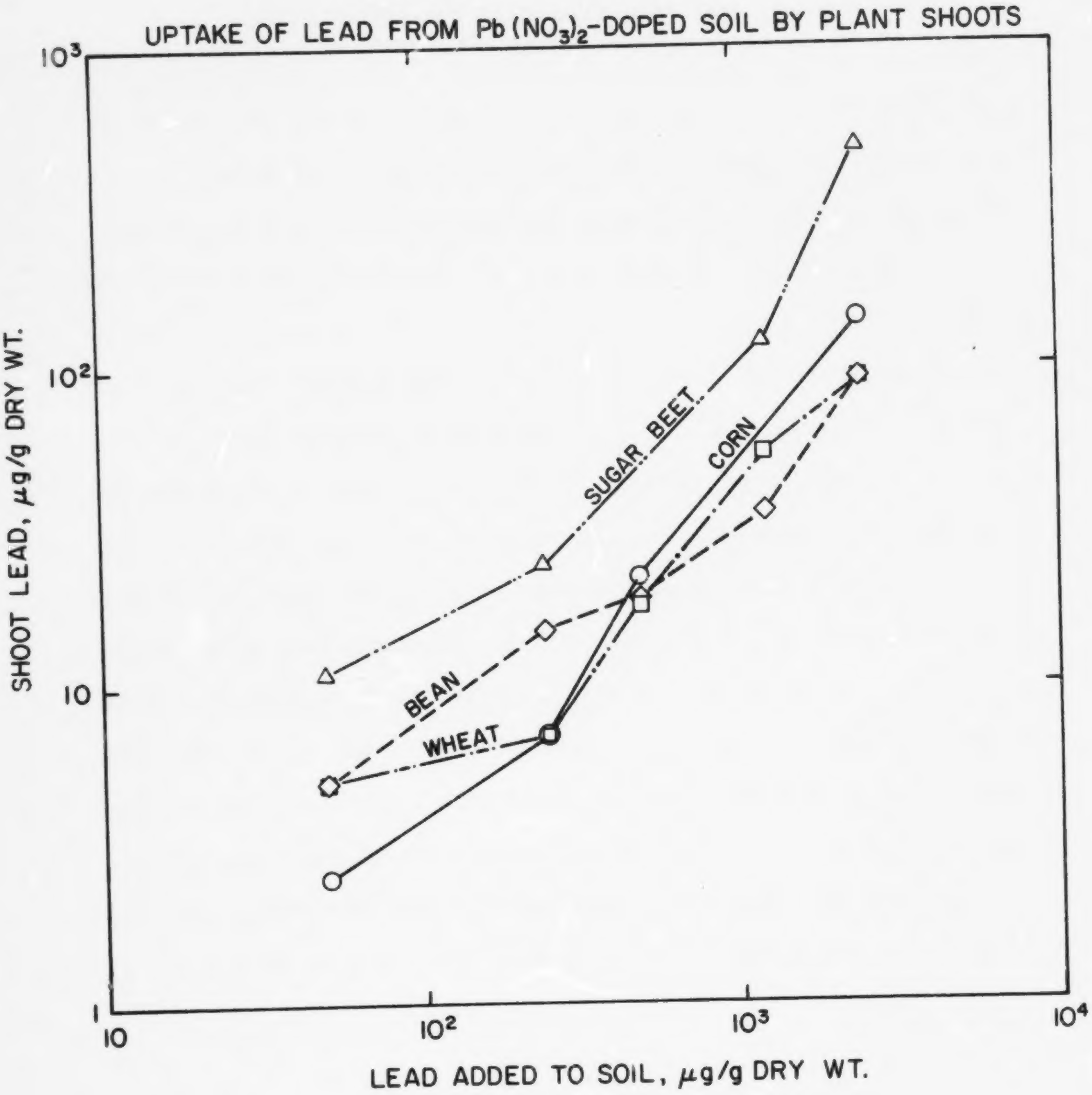

UPTAKE OF LEAD FROM Pb(NO3)2-DOPED SOIL BY PLANT SHOOTS
SHOOT LEAD, μg/g DRY WT.
LEAD ADDED TO SOIL, μg/g DRY WT.
10³
10²
10
1
10
10²
10³
10⁴
SUGAR BEET
CORN
BEAN
WHEAT

Figure 35

IX. TRANSPORT MODEL

A. Introduction

The feasibility of developing an analytical model for short-range environmental transport of automotive lead is being explored. The objectives of this limited modeling effort are the following:

a.) Identify the operant lead transport and accumulation mechanisms in terms of interrelationships.

b.) Characterize the importance and variability of these transport and accumulation mechanisms.

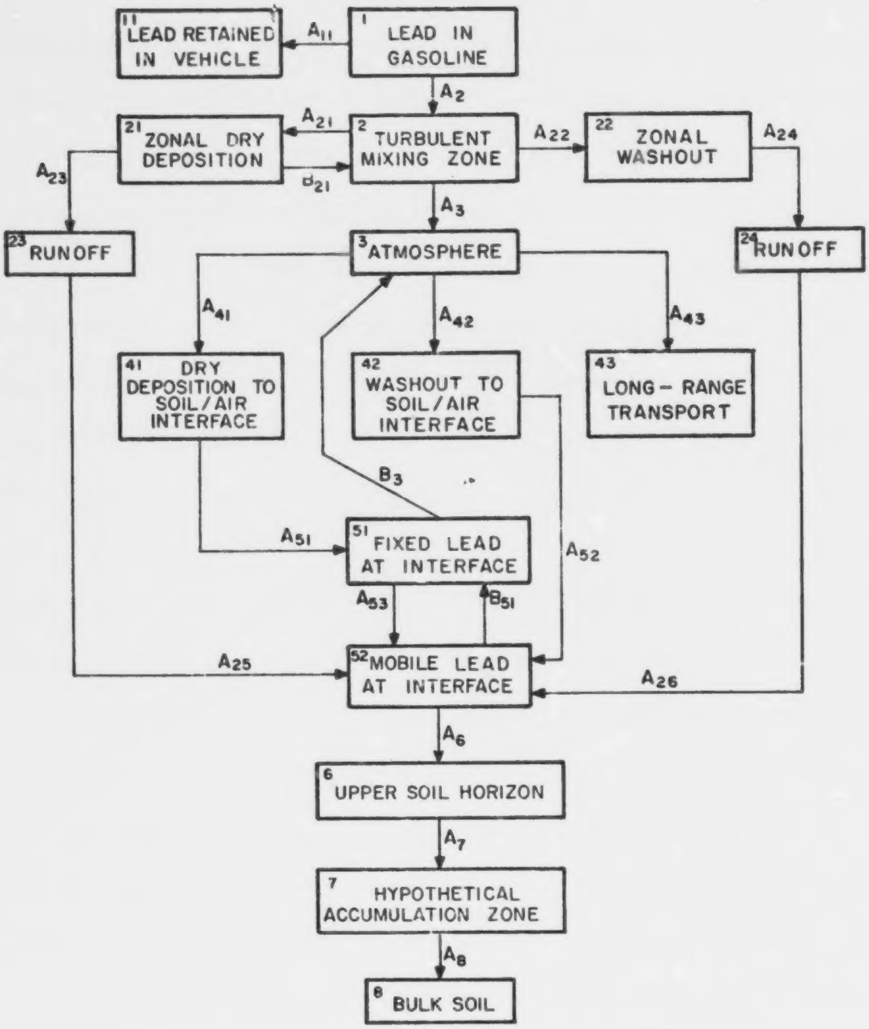
c.) Tie the transport and accumulation mechanisms together in an overall conceptual model and, to the extent feasible, in a mathematical model applicable to other pollutants.

The conceptual model is of value to the interdisciplinary research team in providing an integrated picture of the problem and its components. In terms of measurement of environmental dispersal of automotive lead, the model has also served to indicate to each participant where experimental data from individual research tasks will be utilized. Moreover, the model is helpful in planning and coordinating various research tasks.

The third objective for model development is considerably more quantitative in nature. It is hoped that the model will be of value for predictive purposes. The modeling activity will continue to contribute importantly in tying together the various program segments whether or not quantitation suitable for predictive purposes is attained. It is recognized that high resolution models which include a great deal of environmental realism for transport and accumulation mechanisms may require some sacrifice of generality. The present limited modeling effort should therefore be regarded as an experimental effort in the sense that inclusion of some mechanisms may be hypothetical; their actual importance must be borne out by experimentation in the field. An important benefit to the research team for the present level of modeling activity has been examination of the structure and connectiveness of transport-accumulation interactions by which lead moves from a highway through the environment. Questions regarding the contribution and operation of individual components invariably arise when the model is examined by the group. These questions might not otherwise be addressed and often lead to initiation of individual laboratory or field research tasks.

B. Conceptual Model

The environmental propagation of automotive lead can be traced through the flow diagram in Figure 36 by following the arrows, where forward flow processes are indexed by A_{ij} and reverse flow processes are indexed by B_{ij}. Numbered, enclosed regions denote identifiable states for automotive lead. The system encompasses the region surrounding the highway and extends sufficiently far to include major transport processes. More specifically, the system extends to a height corresponding to the planetary boundary layer, approximately 10^3 m. A lateral extension of 10^4 meters is considered sufficient to include the bulk of gravitational settling effects. The linear extent coincident with the direction of traffic is considered infinite.


11 LEAD RETAINED IN VEHICLE
A11
1 LEAD IN GASOLINE
A2
21 ZONAL DRY DEPOSITION
A21
B21
2 TURBULENT MIXING ZONE
A22
22 ZONAL WASHOUT
A23
A24
A3
23 RUNOFF
3 ATMOSPHERE
24 RUNOFF
A41
A42
A43
41 DRY DEPOSITION TO SOIL/AIR INTERFACE
42 WASHOUT TO SOIL/AIR INTERFACE
43 LONG-RANGE TRANSPORT
B3
A51
51 FIXED LEAD AT INTERFACE
A52
A53
B51
A25
52 MOBILE LEAD AT INTERFACE
A26
A6
6 UPPER SOIL HORIZON
A7
7 HYPOTHETICAL ACCUMULATION ZONE
A8
8 BULK SOIL

FLOW DIAGRAM FOR ENVIRONMENTAL TRANSPORT OF
LEAD FROM TRAFFIC EXHAUST

Figure 36

The conceptual model includes two novel features in terms of environmental transport of particulate pollutants. First, provision is made for gravitational settling and reentrainment of deposited particles in addition to the usual dispersion of very small particles which may be treated as gas molecules. Secondly, atmospheric transport and depletion are coupled to deposition at the soil/atmosphere interface with subsequent soil transport and accumulation. While the present stage of development of the conceptual model does not deal specifically with flora and fauna, the extent to which the presence of flora modify soil uptake and accumulation characteristics is being investigated at the laboratory level. Sufficient flexibility is retained to deal with modifications in soil transport characteristics attributable to plants.

The source strength is defined conventionally in terms of mass/length·time as though the highway constitutes an ideal line source. Departure from ideality can be dealt with by postulating a virtual line source with coordinates displaced from those of the actual source. A variety of meteorological and topographical factors combines to produce departure from ideal line source behavior. Source strength is obtained from measurement of traffic flow and estimation of average gasoline lead content and consumption. Source strength estimates based on total traffic flow measurements mildly overestimate the source strength since diesel fuel does not contain added lead. Adjustment for vehicles consuming low-lead and lead-free gasoline is quite minor in view of their present relatively small share of total gasoline sales. The fraction of lead contained in gasoline which enters the atmosphere can be estimated from previously reported data. However, the effects of altitude and grade may be significant.

It is postulated that ejected lead enters a turbulent mixing zone whose geometry and characteristics are determined by meteorological parameters as well as traffic speed and average spacing between successive cars. In the initial phases of the analytical modeling, it is assumed that crosswinds strong enough to appreciably deform the configuration of the turbulent mixing zone are not encountered. Furthermore, secondary variables such as atmospheric temperature lapse rate, road surface, heat flux, and roughness of the immediate terrain are assumed to be invariant in terms of influence upon the extent of the turbulent mixing zone.

While it is recognized that the chemical and physical nature of automotive lead will undoubtedly affect environmental transport and accumulation processes, these aerosol properties are insufficiently well defined at this time to permit specific quantitative inclusion in the model at its present stage of refinement. Sufficient flexibility is deliberately built into the conceptual model to permit modifications deemed necessary by refinement in the state of knowledge concerning particulate lead. Of particular interest in this regard are changes in particle size distribution and changes in chemical composition with increased atmospheric exposure. Possible electrostatic effects are also of some concern. It has therefore been assumed that the movement of automotive lead through the atmosphere is determined to a major degree by the aerosol settling velocity distribution.

It was recognized from the outset that the actual highway source would not conform to ideal line source behavior for the reasons mentioned above. The existence of a turbulent mixing envelope surrounding the highway was therefore postulated. Turbulence within this zone arises primarily from the motion of traffic. However, laminar flow conditions rarely prevail in the real atmosphere. Mechanically induced turbulence from the traffic flow would normally be expected to be of greater importance than naturally occurring atmospheric turbulence. However, the traffic-induced turbulence would be expected to decay quite rapidly with increasing distance from the edge of the roadway. Therefore, there is a basis for distinction between the character of the atmosphere within the turbulent mixing zone and that existing in the free atmosphere. While this distinction may not be important for describing airborne lead concentrations found many miles downwind from the source, the distinction is believed important for a physically meaningful description of atmospheric lead levels nearby the roadway. This distinction becomes quite important in dealing with depletion phenomena involving relatively large lead-bearing particles. Examples are deposition within the zone both in the presence and absence of precipitation and particle coagulation. Depletion processes occurring within the turbulent mixing zone are therefore distinguished from those that occur outside the zone in the conceptual model.

Airborne lead surviving depletion processes within the turbulent mixing zone is dispersed into the free atmosphere. In the absence of precipitation, further depletion is by gravitational settling. Lead still airborne beyond a lateral distance of 10^4 meters is arbitrarily classified as available for long-range atmospheric transport. The balance of lead, that is, the fraction removed between the boundary of the turbulent mixing zone and 10^4 meters, is deposited at the atmosphere/soil interface. In the presence of precipitation the scheme is modified to include washout. The fraction available for long-range transport may differ under precipitation conditions.

Lead arriving at the interface through dry deposition is arbitrarily designated fixed lead. In the presence of precipitation washed-out lead arriving at the interface is identified as mobile in the sense that it can immediately undergo further environmental transport. Additionally, fixed lead can change in form to mobile lead in the presence of precipitation. The transformation is reversible since under dry conditions mobile lead can revert to fixed lead. The distinction between fixed and mobile lead merits some further comment. It is recognized that the history of lead in the soil may be markedly dependent upon chemical form. A problem is that experimental distinction between adsorption, absorption, and precipitation as immobilization mechanisms is extremely difficult. To facilitate model development in terms of identifiable parameters which are experimentally accessible, a distinction between fixed and mobile lead has been made without regard to chemical form. This distinction applies only in the presence of moisture since all downward transport processes in the soil are dependent upon aqueous mobilization of lead. Further progress of automotive lead from the interface is through the upper soil horizon.
The upper soil horizon may extend in depth to approximately six inches depending upon geographical region, soil type, and nature and extent of vegetation. The line of demarcation occurs upon a marked change in

soil composition. This zone might be encountered where the composition of the soil immediately underlying the upper soil horizon is such that the immobilization capacity for lead is anomalously high. Further transport beyond the hypothetical accumulation zone is through the bulk soil.

Throughout the course of model development considerable reliance has been placed upon input from other participants in the interdisciplinary program. This interaction is sought to insure that the ultimate model will be physically meaningful and to establish the nature of the experimental input that will be used to refine and verify the model. The goals of the modeling effort are therefore intermingled with the goals of the other research tasks.

C. Analytical Formulation

The conceptual model is given analytical formulation through a set of equations which describes the time and space dependent properties of the system in terms of experimentally accessible quantities. Recent applications of systems engineering concepts to model building for ecological systems are exemplified by those examined in the CSU Grassland Biome study (Swartzman, 1970). This document is the result of a series of group workshops concerned with identifying modeling techniques and philosophies which might be applicable to grassland ecosystem modeling efforts. A more recent progress report appeared in July, 1971 (Van Dyne, 1971). The reader is referred to the more recent report on the grassland biome study for a representative treatment of approaches to and problems encountered in modeling ecological systems. A general examination of the problems involved in ecological modeling was made by Patten (1971). Specific examples of applications to smaller scale systems can also be found in Patten. A generalization appropriate for mention at this point is that techniques developed tend to be highly specific to individual problems. Since the primary thrust in the present modeling effort is application of existing techniques rather than development of new modeling techniques, we are in communication with the modelers affiliated with the biome study centered at Colorado State University.

The system of equations is depicted in Table XV. X is the mass concentration of lead in a particular region of the system which may be space and/or time dependent (mass/volume). $\dot{X}$ denotes the first time derivative of the mass concentration of lead in a certain region (mass/volume·time). Y is the mass flux of lead in a particular region of the system which may be time and/or space dependent (mass/area·time). $\dot{Y}$ represents the first time derivative of the mass flux of lead in a given region (mass/area·time^2). A, B are transfer or exchange coefficients which are in general time dependent. After specification of the coefficients, the problem reduces to solution of the system of equations. The method of solution will depend to a large extent upon complexity of the analytical form of the coefficients. In order to apply standard numerical computational techniques, it will be necessary to develop the equations in a matrix form. It is recognized that it may be necessary to sacrifice some environmental realism in order to develop a tractable analytical model. For the first level of attainment for the analytical model, it is desired to interrelate experimentally observed quantities.

TABLE XV

SYSTEM OF EQUATIONS

$\dot{X}_1 = [A_1 - A_{11} - A_2]X_1 = 0$ (1)

$\dot{X}_2 = A_2X_1 + B_{21}Y_{21} - (A_{21} + A_{22} + A_3)X_2$ (2)

$*\ \dot{Y}_{21} = A_{21}X_2 - (A_{23} + B_{21})Y_{21}$ (3)

$*\ \dot{X}_{22} = A_{22}X_2 - A_{24}X_{22}$ (4)

$\dot{X}_{23} = A_{23}Y_{21} - A_{25}X_{23}$ (5)

$\dot{X}_{24} = A_{24}X_{22} - A_{26}X_{24}$ (6)

$\dot{X}_3 = A_3X_2 + B_3Y_{51} - (A_{41} + A_{42} + A_{43})X_3$ (7)

$\dot{Y}_{41} = A_{41}X_3 - A_{51}Y_{41}$ (8)

$\dot{X}_{42} = A_{42}X_3 - A_{52}X_{42}$ (9)

$*\ \dot{X}_{43} = A_{43}X_3$ (10)

$*\ \dot{Y}_{51} = A_{51}Y_{41} + B_{51}Y_{52} - (A_{53} + B_3)Y_{51}$ (11)

$*\ \dot{Y}_{52} = A_{52}X_{42} + A_{25}X_{23} + A_{26}X_{24} + A_{53}Y_{51} - (A_6 + B_{51})Y_{52}$ (12)

$*\ \dot{X}_6 = A_6Y_{52} - A_7X_6$ (13)

$*\ \dot{X}_7 = A_7X_6 - A_8X_7$ (14)

$\dot{X}_8 = A_8X_7$ (15)

$*$ Denotes possible lead accumulation zones

The predictive value of the analytical model will be in its applicability at a variety of locations for a wide range of meteorological conditions. A later level of sophistication would involve prediction of pollutant accumulation with time such as the concentration of lead at the soil/atmosphere interface nearby the highway ten years hence.

1. Atmospheric Transport

Atmospheric transport processes are judged to be the most completely described of the environmental transport interactions depicted in Figure 36. Various atmospheric processes dealt with adequately in the literature include dispersion, washout, gravitational settling, and long-range transport (Slade, 1968). It is intended to rely heavily upon existing analytical expressions for developing coefficients describing atmospheric transport and depletion mechanisms.

2. Current Status

Subject to refinement based on experimental results, the conceptual model is essentially complete. The system of equations for quantitative description has been developed in a generalized form. Present emphasis is upon analytical formulation of the coefficients. Those coefficients which pertain to atmospheric processes are most completely defined in an analytical sense. Noteable exceptions are coefficients involving particle size distribution. Coefficients relating to transport and accumulation processes in the soil are considerably less well developed. While the science of soil physics may be helpful in understanding processes occurring in the soil, it is anticipated that considerable empiricism based on experimental data will be employed to obtain a gross description of soil transport processes. Because the model contains features which enable us to deal with particulate pollutants, the approach should be adaptable to other such substances.

✓

X. ECONOMIC ASPECTS OF AUTOMOTIVE LEAD

A. Introduction

Initial plans call for an examination of social and economic aspects of lead pollution from traffic exhaust in terms of the concepts of benefits and costs (Ogden, 1966). Use of these concepts assumes implementation of some form of control is being considered, and estimation of benefits and costs is useful for a decision in terms of level and type of control. It was recognized at the outset that some aspects of benefits and costs for lead pollution might be incommensurable. It was further recognized that complete quantification might not be feasible. Benefits would be associated with reduction in damage or disamenity, and costs would be associated with goods, services, and activities which would be given up by society to reduce lead pollution. Specifying the nature of benefits would require considerable quantitative information concerning contaminant distribution and physical and biological effects in the environment. Costs are somewhat more clearly identifiable than benefits at this time, and a theoretical and operational analysis has been developed for problems with similar variables (Hartman and Seastone, 1966).

One of the first objectives was therefore to determine whether quantification sufficient to employ a cost-benefit approach could be realized. The starting point for quantification of costs would be a model for the economic structure of the contaminant industry and related industries (Leontief, 1959). For the present example of lead, it would be necessary to consider not only lead mining, refining, and tetraethyl lead production, but also related industries such as those involved with producing lead-scavenging gasoline additives such as ethylene dibromide and ethylene dichloride. Other products which would not be used if lead were to be removed from gasoline would also be considered. The model must include capital equipment and operating costs associated with conversion by petroleum refineries to production of unleaded gasoline. Other markets for lead-oriented products might also be a factor.

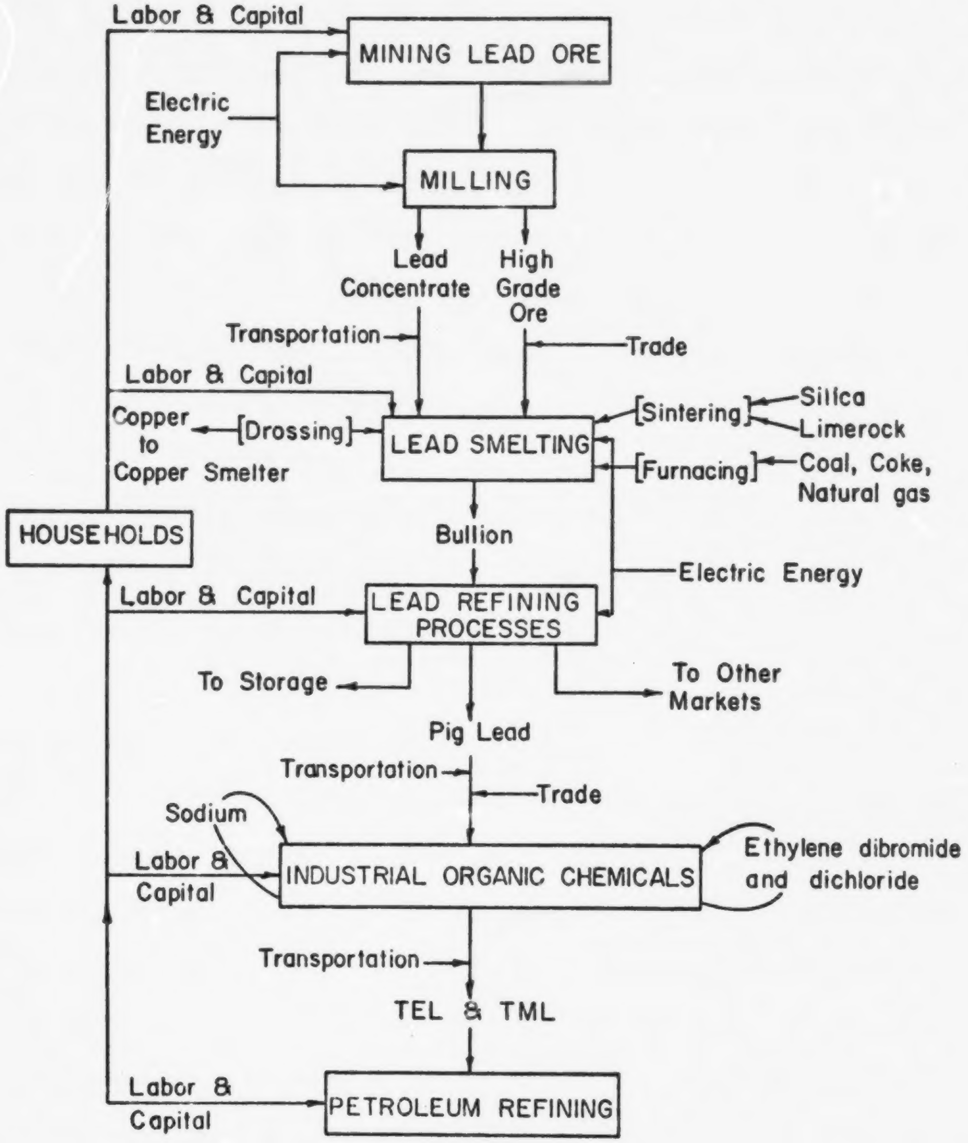
The initial emphasis for the social and economic study has been upon development of a structural model for industrial production of lead alkyls used as gasoline additives. The regional distribution of most of the industries and plants has been identified and provides some basis for estimating the geographic distribution of effects.

B. Production of Lead Antiknock Compounds

Figure 37 depicts some of the more important flows of intermediate goods and services in the production of lead antiknock compounds. There are three main industries involved in the production of lead antiknock compounds: the lead mining industry, smelting and refining, and the industrial organic chemicals industry. It is within these industries that most of the effects would occur. However, there are service sectors such as transportation and trade which would also reflect measurable effects.

Lead occurs in nature principally in the form of sulfide ores (galena, PbS) or oxide or carbonate ores (anglesite, $PbSO_4$, and Cerussite, $PbCO_3$). Minerals of iron, zinc, silver, copper, gold, cadmium, antimony, and bismuth may be associated in varying proportions in these ore deposits.

Domestic mining, smelting, and refining; secondary recovery; and imports are the three main sources of lead in this country. Since World War II


Labor & Capital
MINING LEAD ORE
Electric Energy
MILLING
Lead Concentrate
High Grade Ore
Transportation
Trade
Labor & Capital
Copper to Copper Smelter
[Drossing]
LEAD SMELTING
[Sintering]
Silica
Limerock
[Furnacing]
Coal, Coke, Natural gas
HOUSEHOLDS
Bullion
Electric Energy
Labor & Capital
LEAD REFINING PROCESSES
To Storage
To Other Markets
Pig Lead
Transportation
Trade
Sodium
Labor & Capital
INDUSTRIAL ORGANIC CHEMICALS
Ethylene dibromide and dichloride
Transportation
TEL & TML
Labor & Capital
PETROLEUM REFINING

Generalized Flow Chart for Production of Lead-bearing Antiknock Gasoline Additives.

Figure 37

secondary recovery, the recovery of lead from scrap, has been the largest single source of the lead in the U.S. During 1968 lead-producing mines yielded approximately 359,000 short tons, while 550,879 tons were obtained from secondary recovery. Lead used in gasoline additives and pigments is the only major use of the metal that is not a source of secondary metal recovery. To maximize calculated effects, lead from mines is considered the sole lead source for gasoline antiknock additives.

Milling is required of almost all lead ores except high grade galena and oxide ores that may be amenable to direct smelting. The usual ore-drossing processes are crushing and grinding followed by flotation. Lead concentrate recovered from flotation cells usually contains 45-60% lead. Flotation chemicals are commonly used in this process. The 45-60% lead concentrate will contain varying percentages of zinc, silver, copper, arsenic, and other minerals originally in the mined crude oil. Transportation of ore or concentrate from the mine or mill to the smelter is an important cost paid by the miner.

The only method currently employed in the United States to extract metallic lead from its ores is smelting in a blast furnace followed by various refining processes. Blast furnace smelting consists of three main steps: (1) sintering (sulfur elimination); (2) furnacing (reduces oxidized lead to 95% lead bullion); and (3) drossing (removes copper compounds from the bullion). Smelter recovery of lead from lead concentrate varies from 96-99%. In terms of production costs at smelters, the cost of concentrate is the largest single expensive item. Labor is the second largest item.

Removal of impurities from bullion obtained from complex ores mined in the western states is both necessary and profitable. Refining consists of the following operations: (1) softening (removal of metal oxides); (2) desilverizing; (3) dezincing; (4) final refining (adding sodium hydroxide) to remove remaining traces of impurities. After refining, the lead is cast into pigs or blocks weighing from 100 pounds to one ton for transportation to market or storage prior to processing into fabricated products.

One market for pig lead is production of lead-containing antiknock compounds for gasoline. After batteries, it represents the second largest consumption outlet for lead. TEL, a colorless fluid containing 64% by weight lead, is the principal active ingredient in antiknock compounds, but TML has become increasingly more popular. Use of these compounds is of great interest to the primary lead producer because these products are totally dissipated.

Antiknock compounds are used to improve octane ratings of over 98% of all gasoline produced in the United States. One gallon of premium gasoline contains 3 to 4 cubic centimeters of TEL compared with 0.5 to 1.5 cubic centimeters in regular gasoline. The maximum TEL content in gasoline allowed by law is 4 cubic centimeters per gallon.

Antiknock fluid is manufactured from the following chemicals: sodium, lead, ethyl chloride (TEL) or methyl chloride (TML), ethylene dibromide, and ethylene dichloride. The reaction takes place in the presence of a catalyst.

Lead consumption during 1968 in the manufacture of TEL and TML was about 525,000,000 pounds. The 1969 forecast for the manufacture of TEL and TML is 720,000,000 pounds, with a predicted growth rate of about 3%

per year for the next five years.

Manufacturers and cities for the manufacture of TEL and/or TML are:

(1) Ethyl Corporation......................Baton Rouge, Louisiana
and Houston, Texas
(2) E. I. du Pont de Nemours & Co., Inc. ...Deepwater Point, N.J.
and Antioch, California
(3) Houston Chemical.......................Beaumont, Texas
(4) Nalco Chemical.........................Freeport, Texas

Statistics on the number of production workers and tonnage production per TEL plant can only be approximated. For example, at its Baton Rouge plant, Ethyl Corporation has approximately 2,100 employees in its Manufacturing Department in addition to sizable numbers in Research and Development Engineering Departments; at Houston nearly all of its 1,000 employees are engaged in manufacturing. However, both plants manufacture several chemicals other than antiknock agents, e.g., sodium, hydrocarbons, and polyvinyl chloride. Also, a diversity of products is manufactured by du Pont at its Deepwater Point plant. Industrial organic chemicals sells TEL and TML to the petroleum refining industry as shown in Figure 37.

C. Input-Output Analysis

The objective is to predict unemployment and income effects for various industrial sectors which would result from reduction or elimination of the use of lead in gasoline. These effects reflect social costs in as much as there are costs to the unemployed for moving to new jobs, retraining, and so forth. Also, there is complete immobility in some capital facilities. For example, specialized equipment for processing of tetraethyl lead might be scrapped in the event of the removal of lead from gasoline. In the present phase of the study, we make no attempt to estimate the actual social cost resulting from a reduction in the use of lead but only estimate the unemployment and reduction in payments of income to capital and labor as indices of the costs.

1. Mechanics of the Input-Output Model

The initial tableau in developing the model consists of flows, as discussed with reference to Figure 37. A flow table for a two-sector model is presented below. Final demand is most specifically defined as the exogenously determined, or outside, variable affecting the system under study. In the lead study, final demand would consist of shipments of lead compounds to the petroleum industry.

	(1)	(2)	Final demand	Total
(1)	x_{11}	x_{12}	Y_1	X_1
(2)	x_{21}	x_{22}	Y_2	X_2

The basic relationship of the set of accounts is that $Y_1 = X_1 - x_{11} - x_{12}$. Given the x_{ij}'s and the X_i's, the manipulation of these data proceeds by deriving coefficients, $a_{ij} = \frac{x_{ij}}{X_i}$. It will be observed that $x_{ij} = a_{ij}X_i$, so the basic set of equations of the model can be stated from the previous table, as set out below.

$$X_1 - a_{11}X_1 - a_{12}X_2 = Y_1$$
$$X_2 - a_{21}X_1 - a_{22}X_2 = Y_2$$

This statement of the set of accounts indicates that total sector output minus intersector shipments equals final demand.

The matrix multiplication form of the equations, which is implicit in most tabular presentations, is as follows:

$$\begin{bmatrix} 1 - a_{11} & - a_{12} \\ -a_{21} & 1 - a_{22} \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \end{bmatrix} = \begin{bmatrix} Y_1 \\ Y_2 \end{bmatrix}$$

And in matrix notation we denote this multiplication as $(I - A)X = Y$, where $(I - A)$ represents the $(1 - a_{11})$, $-a_{12}$, etc. matrix, X represents the output column vector, and Y the final demand column vector.

The solution involves deriving a system of equations where the X's are functions of the Y's, i.e., the X's become weighted sums of Y's. The set of coefficients consistent with this statement is derived, for a large matrix, by the process known as inversion and the inverse coefficient matrix is denoted as $(I - A)^{-1}$. Thus the solutions statement is $X = (I - A)^{-1}Y$ and the total output levels, X's, can be determined for any level of Y's. The form of the solution equations for the two-sector example is set out below.

$$X_1 = C_{11}Y_1 + C_{12}Y_2$$
$$X_2 = C_{21}Y_1 + C_{22}Y_2$$

The C's are the inverse or interdependency coefficients. The diagonal C_{ij}'s, $i = j$, will be equal to or greater than one and all other C_{ij}'s will be less than one. In our example, the C_{11} indicates the amount of increase in total output of sector (1) necessary to increase deliveries to final demand by one dollar. The coefficient will be greater than one by the amount of own inputs used in the production process of sector (1) and the amount of sector (1) output used by sector (2) to produce its output, which is used by sector (1) as input. The C_{21} coefficient represents the increase in output of sector (2) for every dollar increase in deliveries to final demand of sector (1).

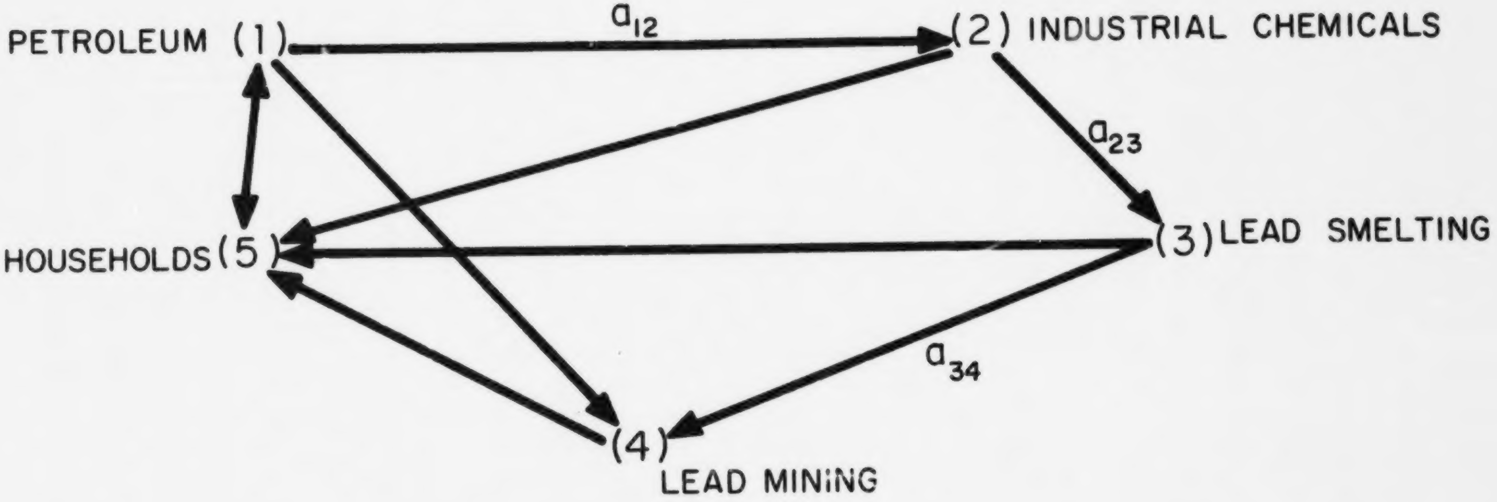
The C_{ij}'s are commonly referred to as sector multipliers. That terminology is used in this report. The column vectors are arrays of multipliers for each sector. In the estimation of effects for reducing the use of lead in gasoline, the industrial chemicals sector in the inverse matrix is the relevant column of multipliers since it is from that sector that shipments to final demand, the petroleum industry, occur. Column (1) in Table XXV lists the multipliers (C_{ij}'s) for that sector.

2. Analysis

Figure 38 depicts the flow of goods and services (and therefore implicit payments) among concerned industrial sectors and households. The petroleum industry (1) purchases a_{12} of tetraethyl lead from the industrial chemicals industry (2), which in turn purchases a_{23} of lead from the lead smelting industry (3). The lead smelting industry purchases a_{34} lead from the lead mining industry (4). All four sectors also purchase from other sectors and purchase capital and labor services from households (5). Households (the consumers) purchase gasoline from the petroleum industry. This is indicated by the two-way arrow. The a_{ij}'s are dollar value of inputs per dollar of gross output of each industry. For example, a_{12} is the dollar amount of tetraethyl (and tetramethyl) lead per dollar's worth of gasoline output. If the petroleum industry were to change to a fuel which did not use lead, then the effect per dollar of output can be traced back through the flow diagram.

Figure 38

FLOW OF GOODS AND SERVICES AMONG SECTORS
CONCERNED WITH LEAD


PETROLEUM (1)
a_{12}
(2) INDUSTRIAL CHEMICALS
a_{23}
HOUSEHOLDS (5)
(3) LEAD SMELTING
a_{34}
(4)
LEAD MINING

All of the four sectors, lead mining, lead smelting and refining, industrial organic chemicals, and petroleum refining, purchase capital and labor services from households. Households, as consumers, in turn purchase gasoline from the petroleum refining industry. This is indicated in Figures 37 and 38 by the two-way arrow.

The flows in Figure 38 are economic ones based on interindustry transactions, i.e., an exchange relationship where goods and services are purchased. Therefore, the prediction of changes in some of the transactions resulting from an exogenous change in others is subject to considerable uncertainty due to a lack of knowledge of all details of present and future business relationships. The initial exogenous change, of interest to this study, would be to diminish or eliminate the sale of tetraethyl lead from industrial organic chemicals to petroleum refining. The first order of effects resulting from this change would be a reduction in transportation inputs, a reduction in capital and labor inputs into the industrial organic chemicals industry and so on back up through the indicated transactions of Figure 37. We have only listed the more important flows. The problem is somewhat more complex. One area of weakness in the data presented in this report and also in the figure is that there are several supply sources of lead for the industrial organic chemicals sector when we show only one--domestic mining and its related industry complexes. As indicated earlier, reprocessing of lead and foreign imports are important supply sources. The interindustry effects would be somewhat different between each of these supply sources, and our data are inadequate to specify which supply source is presently used, and more importantly, which one would be affected were industrial chemicals to reduce purchases.

The interindustry effects originate with the industrial chemicals sector since it sells the final product to the petroleum industry. Estimates resulting from "shutting off" these sales have been prepared and are summarized in Table XVI. The income effect would be approximately $317 million; the wage effect would be approximately $87.7 million. For these industry segments the capital effect would be $234 million. The unemployment effect in industrial organic chemicals and related service industries would be 11,880. A regionality breakdown estimate for the lead smelting industry is given in Table XVII.

The above calculated effects do not represent social costs; they are social indicators. Costs, particularly those to individuals, result from immobilities and transfer or retraining. One could expect many of these changes to be absorbed except for some possible local effects with which the continuing work deals. However, some of the effects on payments to capital would constitute costs since the capital facilities are specialized to lead and could therefore be obsolete and cease to earn income.

TABLE XVI

ESTIMATES OF THE EFFECT TO THE INDUSTRIAL ORGANIC CHEMICALS INDUSTRY FROM THE ELIMINATION OF LEAD FROM GASOLINE

Sector (1)	Sector Multipliers (2)	Income Multipliers (3)	Income Effect ($1,000) (2)X(4X10^8) (4)	Wage Multipliers (5)	Wage Effect ($1,000) (5)X(4X10^8) (6)	Capital Multipliers (3)-(5) (7)	Capital Effect ($1,000) (4)-(6) (8)	Employ. Multip. (9)	Employ. Effect (Numbers) (9)X(4X10^8) (10)
1. Indust. Org. Chem.	1.1961	.6788	271,520	.1776	71,040	.5012	200,460	.0228	9,120
2. Lead Smelting & Refining	.0106	.0071	2,840	.0046	1,840	.0025	1,000	.0009	360
3. Lead Mining	.0107	.0010	400	.0006	240	.0004	160	.0001	40
4. Petrol. Refining & Related Prods.	.1056	.0208	8,320	.0061	2,440	.0147	5,380	.0008	320
5. Crude Petrol & Nat. Gas	.0617	.0475	19,000	.0054	2,160	.0421	16,840	.0008	320
6. Chem. & Fert. Minerals	.0341	.0256	10,240	.0081	3,240	.0175	7,000	.0012	480
7. Blast Furnace, Steel Works & Milling	.0235	.0106	4,240	.0051	2,040	.0055	2,200	.0007	280
8. Trans. -- R. R. & Rel. Motor Freight Water Transp.	.0265 .0125 .0109	--	--	--	--	--	--	--	--
9. Electric, Gas, Water & Sanitary Services	.0296 .0503 .0048	--	--	--	--	--	--	--	--
10. Wholesale Trade	.0428	--	--	.0022	880	--	--	.0004	160
11. Real Estate	.0330	--	--	--	--	--	--	--	--
12. Misc. Bus. Services	.0218	--	--	.0080	3,200	--	--	.0018	720
13. Advertising	.0137	--	--	.0016	640	--	--	.0002	80
TOTALS			316,560		87,720		233,560		11,620

[--] data not available

TABLE XVII

EMPLOYMENT LOSSES BY CENSUS REGIONS, LEAD SMELTING INDUSTRY*

Sector	New England	Middle Atlantic	E.N. Central	W.N. Central	South Atlantic	E.S. Central	W.S. Central	Mountain	Pacific	TOTAL
1. Primary Lead	--	--	3	16	2	--	8	23	8	60
2. Nonferrous Metal Ores Mining	--	--	--	35	9	16	8	341	25	434
3. Industrial Chemicals	1 1	9	8	2	7	3	9	1	2	42
4. Primary Zinc	--	33	14	1	5	28	33	31	--	145
5. Primary Aluminum	--	2	2	--	1	3	7	1	4	20
6. Primary Nonferrous Metals N.E.C.	1	5	6	--	0	2	6	1	4	25
7. Secondary Nonferrous Metals	10	136	144	12	20	11	20	3	44	400
8. Transp. & Warehousing R.R. & Motor	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
9. Wholesale Trade	2	9	8	4	5	2	4	1	5	40
10. Real Estate	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

*The employment effect in the lead smelting industry was spread among the regions according to the original percent of employment in each sector.

D. Benefits

Quantification of benefits to society accruing from discontinuance of the use of lead antiknock compounds in gasoline may not be practical. In addition to the difficulty of incommensurability, some aspects of damage reduction attributable to cessation of combustion of leaded gasoline have not been identified. There is little scientific agreement concerning the nature and extent of such damages. Furthermore, any such analysis must also take into consideration consequences of damages associated with combustion of substitute fuels. Damages associated with combustion of leaded gasoline have received little scientific study, and damages associated with combustion of substitute fuels have received essentially no scientific study. While some quantification of the economic aspects of lead intoxication has been attempted (Lutz et al., 1970), there is general agreement in the scientific community that lead from traffic exhaust contributes only negligibly if at all to urban plumbism. In the Battelle Memorial Institute study benefits were associated with reduction in expenditure of resources for treatment of individuals suffering lead poisoning, and costs were those associated with eliminating and correcting substandard housing in which use of lead-containing paint and putty is widespread. Even this very gross type of analysis would be inappropriate for estimating beneficial aspects associated with removal of lead from gasoline since consequences for combustion of substitute fuels are virtually unknown.

A second approach which could be taken is to agree that pollution reduction is of benefit to society for its own sake. With that stipulation it is possible to contrive an index for ranking various approaches to reducing pollutant production. Such an approach was employed by participants in an Air Pollution Control Association meeting devoted to consideration of approaches to control of automotive emissions (Air Pollution Control Association Preprints, 1970). The pollutants considered were oxides of nitrogen, hydrocarbons, and particulate matter. Lead was not dealt with specifically. To develop such an index for economically ranking various approaches to reducing lead pollution, one would first stipulate that the desired result is the greatest reduction in lead pollution at least overall cost. It would then be necessary to develop a set of ground rules which would be agreeable to proponents of various alternatives for reducing lead pollution. The approach yielding the greatest reduction in lead pollution at least cost would then be declared the "best" approach. The APCA study of the above three pollutants was revealing, but there was little agreement among participants concerning the so-called best approach in spite of the obvious emergence of a quantitative winner. A similar effort might prove a worthwhile and illuminating endeavor for lead pollution. One major difficulty, however, might be in obtaining agreement concerning the original premise.

A third approach to estimating economic aspects of benefits associated with pollution reduction is that employed by Gilmore (1971). In this study the petroleum refining industry is analyzed to identify major pollution-producing sectors. Quantification of pollution production is given through use of input-output data. Conversion of input-output data to pollution-production data for each sector is accomplished through a detailed study of industrial processes employed in product manufacture. The final step in the analysis involves use of the pollution-production data for comparing public policy alternatives that are available for pollution reduction.

Other approaches to quantification deal with increased consumer costs associated with replacement of leaded gasolines with low-lead and lead-free gasolines of comparable antiknock properties. Industry estimates for the overall consumer cost increase range between 2-5¢ per gallon (Fuller, 1971). An EPA-sponsored economic study of the cost of removing lead from gasoline was conducted by Bonner & Moore Associates, a Houston, Texas, consulting firm (Bonner & Moore, 1971). That study indicates motorist cost for lead-free gasoline will be between 5.5-7¢ per gallon. EPA's own estimate for the direct cost of lead removal is considerably lower, 0.2-0.9¢ per gallon. The major discrepancy between the two sets of figures arises from lack of agreement between EPA and Bonner & Moore Associates concerning what constitutes cost. Bonner & Moore Associates took into account added manufacturing and distribution costs as well as income losses resulting from equipment obsolescence. Also included in the Bonner & Moore analysis are costs associated with lower crude-to-feedstock conversion efficiency and higher energy requirements associated with the need for more catalytic reforming for production of fuels of adequate antiknock quality in the absence of lead. The Bonner & Moore study also indicates that future emission control devices and lower compression ratios will reduce engine efficiency about 12% which will result in indirect cost increases of 4-5¢ per gallon. According to the Ethyl Corporation, use of lead antiknock compounds is equivalent to an annual petroleum conservation of about

250 million barrels of oil in the U.S. (Chemical Week, December 24, 1969).

At the present time none of the above approaches is directly applicable to estimating benefits associated with removing lead from gasoline. Attempts to obtain quantification for damage reduction aspects have therefore been deferred. One approach that might be fruitful would be to stipulate that the greatest societal benefit to be derived from removing lead from gasoline would be to prevent deactivation of catalytic pollution control devices. Quantification could then proceed along the lines of the APCA West Coast Section approach referred to above.

E. Societal Action

Social concern for lead in the environment focuses upon effects of lead on things of human value and consequences of reducing lead use. This study is concerned primarily with leaded gasoline as a source. Reducing the use of leaded gasoline may appreciably reduce the influx of lead into the environment. Moreover, elimination of lead in gasoline may contribute to development of effective and inexpensive methods for control of other automotive emissions. One basis for rational public action would include evaluation of benefits and costs resulting from decreasing this use of lead. Benefits associated with reduction in damages would include improved health, longer life, improved enjoyment of life, and reduced medical costs, which would be reflected as physical effects on individuals. Other benefits associated with economic good might be improved crop yields and longer life for animals. Costs associated with curtailing the use of lead in gasoline would include increased cost of transportation and increased costs associated with production of lead-free fuels. While costs can be estimated by means of the input-output analysis formalism discussed previously, benefits resulting from damage reduction are insufficiently well described at this time to permit such quantification. A further difficulty is that the impact of major changes in the use pattern of lead antiknock additives might vary considerably among various interest groups and classes within society on the basis of their relation to the lead problem. We are exploring the relation of the lead problem to various classes and groups within society in terms of consequences specific to each resulting from various alternative social action decisions regarding the use of lead in gasoline.

No fully satisfactory method of analysis presently exists by which decision makers can quantitatively evaluate alternatives for societal action on issues relating to environmental quality. While input-output analysis is one obviously important aspect of such an analysis, it is unsuitable where important aspects of benefits are incommensurable or unidentifiable. The lead pollution problem is typical of a class of socio-economic problems in what is called the theory of public goods or of social choice in the literature of economics. The term "goods" in this context does not mean tangible, physical commodities but rather aspects of living which are valued and, also, scarce in the sense that it takes resources to provide them. The term "public" means that the goods are provided for everyone and managed by means of some form of collective control. The characteristics of historically provided collective goods vary in terms of the grounds or justification for being provided publicly. Health and education, for example, as public goods can be justified on the grounds they provide collective benefits beyond that of the individual and which he therefore would not be willing to pay for as an individual. Some goods have the characteristic that if anyone is to have the good everyone must have it, and it is difficult for individuals to voluntarily contribute to the provision of the good as individuals. Environmental quality would fit into this latter category although it has some aspects of the other category also.

The economists' study of the demand for private goods has not progressed beyond the attempt to specify revealed preference as the basis of any theory of consumption behavior. This theory has assumed that increasing levels of consumption represent increasing levels of well being by definition. These economists have also been reluctant to make interpersonal generalizations, assuming that one man's meat could be another man's poison and that it was beyond the scope of positive science to develop theory and empirical data on that relationship. It is obvious that revealed preference is virtually impossible to express or measure with respect to public goods. Some public goods are specifically provided to counteract the preferences of some individuals. Attitudes regarding most goods are difficult to express prior to experiences so that polls and interviews are inadequate instruments for measuring demand or preference.

There is need to extend the social science aspects of the lead pollution study into the areas of social choice and identification and explication of the value-preference-welfare characteristics of a class or problems exemplified by lead pollution. Continuing work deals with the decision process itself and the kind of objective criteria, not necessarily quantitative, relevant to the choice process. Both aspects of the problem are interrelated and must be considered simultaneously. It is thus hoped to provide evaluation criteria for both the decision process and for quality of life considerations involved in pollution problems.

XI. CENTRAL ANALYTICAL SERVICE

A. Introduction

The central facility for chemical analysis of project samples became operational in August, 1970. We believe that there are three primary advantages to such a laboratory. First, the work is handled by individuals whose primary interest and training are in analytical chemistry. This should result in improved overall operation. While non-analytical chemists can do analysis, analysis is of generally secondary interest, and these individuals are less likely to be aware of the latest developments and requirements in the field.

By centralizing the analysis program, quality control procedures can be adopted that would not be practical for a fragmented operation. Quality control is absolutely necessary to be sure of repeatibility and reliability of chemical analyses. Centralized laboratories are also useful in avoiding unnecessary duplication of equipment. Ideally, a centralized service for chemical analysis will involve lower costs than analytical capabilities dispersed over the university campus.

The primary analytical capability for soil samples is direct emission spectrographic analysis which may be expanded to include some plant and animal samples. Atomic absorption spectrometry is the primary analytical capability for most other samples. Both techniques have been tested by quality control procedures and found to be generally satisfactory. Groups of blood and plant samples have been sent to A. M. Hartley (Illinois) and S. R. Koirtyohann (Missouri) for comparative analyses. As of June 1, 1971, over 1500 samples have been subjected to chemical analysis at the central analytical facility.

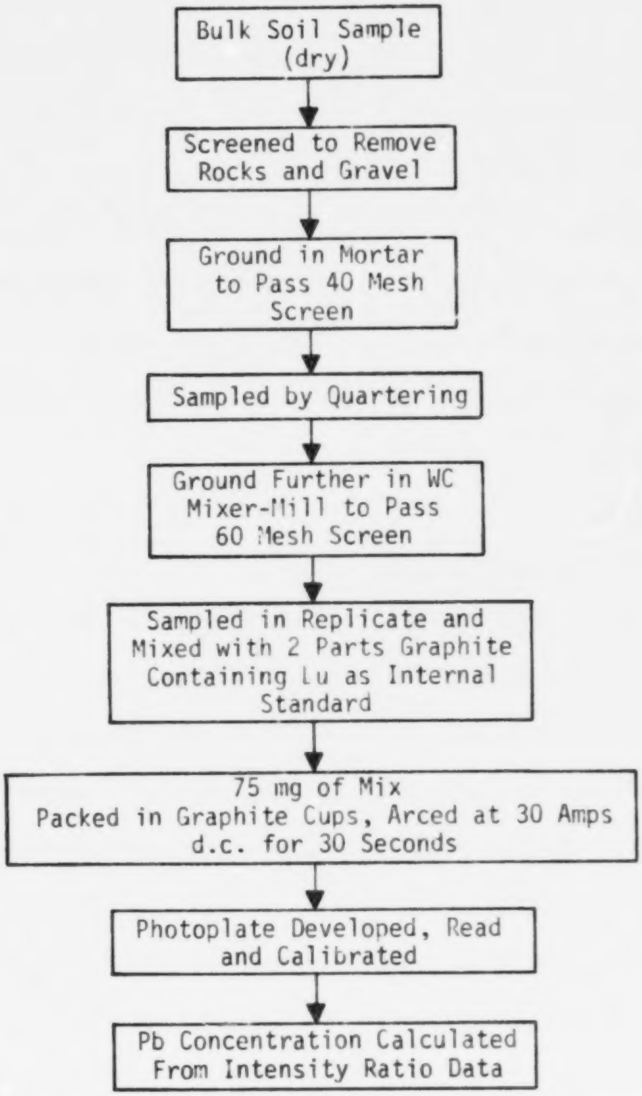
In response to the need for measuring quantities of lead that may range down to a nanogram, a microwave excitation method has been devised which provides a reproducibility of ±10% of the amount present at the 5 nanogram level. Also being explored is possible use of the AAS sampling boat technique to supplement analytical capabilities at low concentration levels.

B. Soil Samples

Soil samples are analyzed for lead by two techniques. Emission spectroscopy has been selected as the primary method with AAS being used as a support method. The details of the analytical techniques are given below.

1. Emission Spectroscopy

The high current density d.c. arc technique developed by Bedrosian, Skogerboe, and Morrison (1968) for biological samples is also advantageous for soil samples. In addition to the high degree of sensitivity that may be realized, high current densities appear to eliminate problems which may stem from changes in the general composition of different soil samples, e.g. matrix effects. A flow chart for the emission spectrographic method is given in Figure 39. Each sample is analyzed at least in duplicate, and the average result is reported. If replicate results are not in good agreement the samples are rerun. This happens rarely. Concentrations ranging over three orders of magnitude from less than 1 ppm to several thousand ppm can be handled directly without prior concentration. Calibration curves for the two analytical lines employed are shown in Figure 40. Moreover, a permanent photographic record is obtained which can be used to determine other elements in the soil at a later date.


Bulk Soil Sample (dry)
Screened to Remove Rocks and Gravel
Ground in Mortar to Pass 40 Mesh Screen
Sampled by Quartering
Ground Further in WC Mixer-Mill to Pass 60 Mesh Screen
Sampled in Replicate and Mixed with 2 Parts Graphite Containing Lu as Internal Standard
75 mg of Mix Packed in Graphite Cups, Arced at 30 Amps d.c. for 30 Seconds
Photoplate Developed, Read and Calibrated
Pb Concentration Calculated From Intensity Ratio Data

FLOW CHART FOR EMISSION SPECTROGRAPHIC METHOD FOR LEAD IN SOIL
Figure 39

CALIBRATION CURVES FOR DETERMINATION OF LEAD
BY EMISSION SPECTROGRAPHY

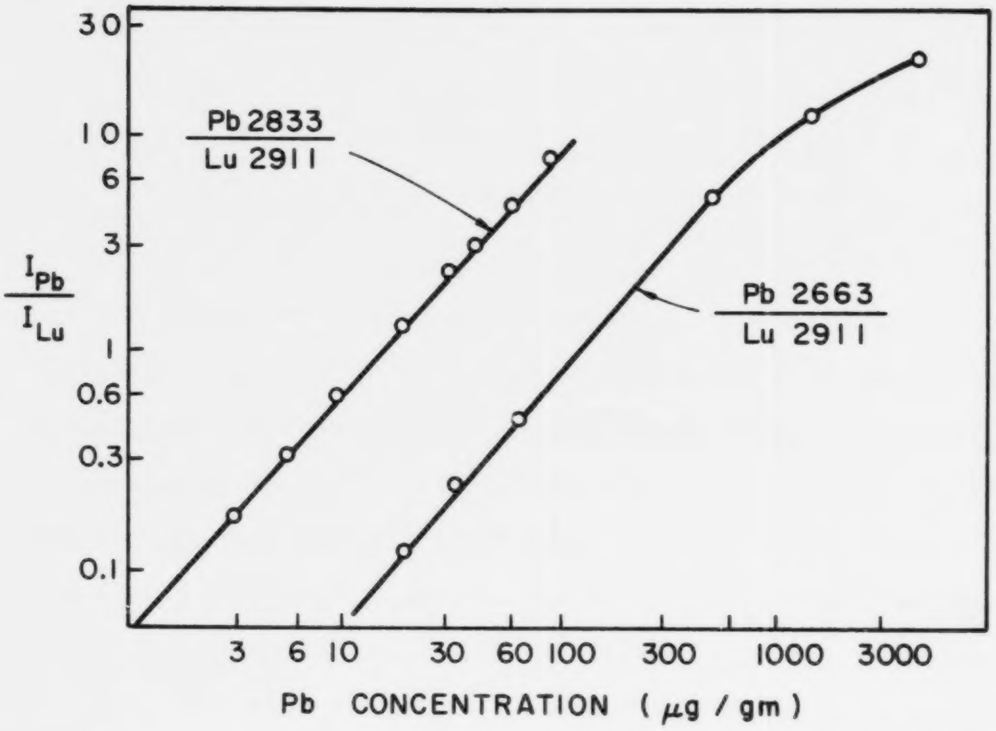


Figure 40

To establish the analytical reproducibility of the technique, pooled standard deviation estimates have been calculated for replicate soil samples that fall into different concentration ranges. The results presented in Table XVIII indicate that the analytical precision is consistently about 12-13% of the amount present at all concentration levels.

TABLE XVIII

PRECISION OF THE METHOD

Concentration Level, ppm Pb	Relative Standard Deviation
20 - 30	12.9%
600 - 800	12.2%
1500 - 2000	12.7%
20 - 2000 (overall average)	12.6%

Uncertainty in a reported analytical result can also arise from variations in sampling technique as well as in the method of chemical analysis. To determine the relative importance of each contribution it was assumed that all soil samples collected at the 30-36" depth at a distance of at least forty feet from the highway were baseline samples uncontaminated by lead from traffic exhaust. Variations among samples would thus provide a quantitative measure of the natural variation. A summary of the statistical analysis is given in Table XIX.

TABLE XIX

SOURCES OF VARIATION IN SOIL ANALYSIS

Source of Variation	s^2	s	s, %
Analysis technique	8.74	2.95	12.9
Sampling	10.93	3.30	14.4
Analysis plus sampling	19.67	4.43	19.3

Contributions to total uncertainty by uncertainty in chemical analysis and variations in sampling are 12.9% and 14.4% respectively. Approximately half of the total variation observed is due to the natural variation in the soil which may be classified as a sampling error. The remainder is due to the analytical technique itself. We can therefore expect an approximately ±20% variation in a reported analysis due to the combined effects of sampling and analysis errors.

The average (baseline) lead concentration in soil calculated by the above method is 22.9 ± 4.4 ppm. The calculated 95% confidence limits are 14.1 and 31.7 ppm. It is therefore likely that soil samples having lead concentrations above the latter value are contaminated.

The following question therefore immediately arises: Is the surface soil contaminated with reference to the baseline value at distances greater than forty feet from the highway? Based on analysis of surface and subsoil samples beyond forty feet, the mean surface value is 31.9 ± 4.4 ppm, and the subsoil value is 19.3 ± 3.6 ppm. A student t value computed from these data is 2.25 which is less than the required value of 2.34 at the 95 % confidence level. However, the difference is significant at the 90% confidence level. While the above computations are based on samples averaged over a six inch soil depth beyond forty feet from the highway, samples collected very near the highway do show a large concentration gradient within the first six inches of penetration. These data are discussed in the next section dealing with lead in soil. It must therefore be concluded that the ability to distinguish between surface and subsoil concentrations depends to some extent upon the definition of the surface region.

2. Atomic Absorption

Soil samples to be analyzed by atomic absorption spectroscopy are ground to pass a 40 mesh screen. The sample is then digested in hot concentrated nitric acid for one hour or more, and the undissolved residue is then removed by filtration. The residue is washed again with hot nitric acid. Emission spectrographic analysis of the washed residue indicates that more than 99% of the lead is removed by this approach. The filtrate is then diluted to volume with 3 molar nitric acid and analyzed using an air acetylene flame.

In the atomic absorption determination of lead, background absorption due to light scattering and/or molecular absorption presents a problem which requires correction. The total absorbance is first measured at the lead analytical line using a hollow cathode lamp. Background contribution is then determined using a continuum lamp. Scattering and absorption from a digested blood sample are shown in Figure 41.

SCATTERING AND MOLECULAR ABSORPTION FROM A DIGESTED BLOOD SAMPLE

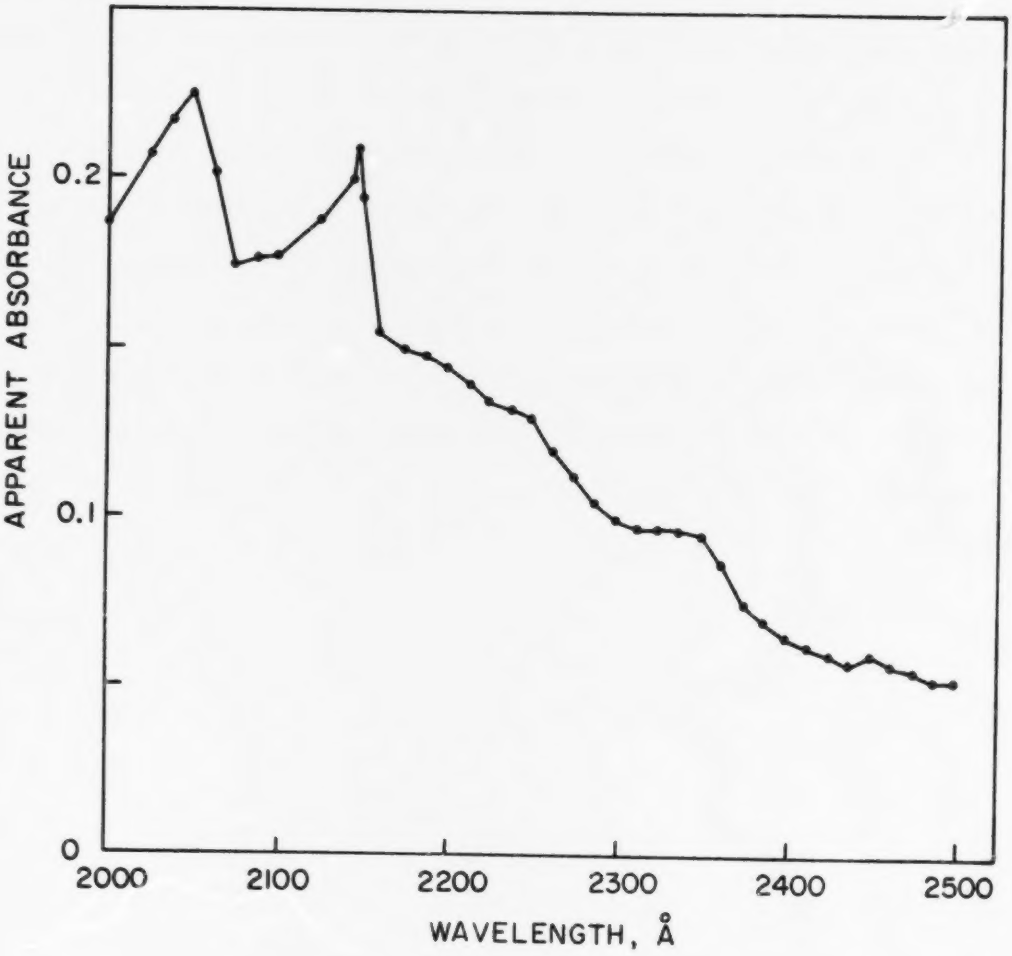


Figure 41

3. Comparison of AAS and Emission Techniques

Identical soil samples have been analyzed by both the emission and atomic absorption techniques for purposes of comparison. The data presented in Table XX indicate that the methods agree within the limits of variation discussed above, e.g. ±20%. Sample 40-13 is an interesting case in that it was a surface sample taken very near the highway which contained relatively large amounts of fine gravel and tar. The sample was sieved into the screen sizes indicated in Table XXI , and each fraction was analyzed separately for lead. These results indicate that lead has a pronounced tendency to concentrate in the finer soil fraction. Calculation of a weighted average concentration gives a value of 1180 ppm which verifies the earlier AAS analysis. We have since adopted a quartering method of sampling which largely eliminates this source of error for emission spectrography (for example, see 3/6/71 data).

TABLE XX

COMPARISON OF EMISSION SPECTROGRAPHY VS. ATOMIC ABSORPTION ANALYSIS OF Pb IN SOIL

Sample Number	ppm by Atomic Absorp.	ppm by Emisssion Spec.	% Difference
40-1 (2/5/71)	300	260	-14.3
40-1 (2/16/71)	316	260	-17.7
40-2	150	180	+18.0
40-7	250	200	-22.2
40-8	84	63	-28.8
40-13* (2/5/71)	1130	1900	+50.0
40-13** (3/6/71)	1150	1300	+13.0
40-14	1120	1200	+ 7.1
40-19	1300	1600	+20.7
40-20 (2/5/71)	980	900	- 8.2
40-20 (3/6/71)	970	900	- 7.2
3-1	395	370	- 3.8
3-2	172	190	+ 9.5
3-3	72	93	+22.6
3-4	67	63	- 6.0
3-11	33	37	+ 8.3
7-2	37	50	+26.0
7-5	20	28	+28.6
14-2	540	610	+13.0
14-11	1190	950	+20.1
14-14	1270	1250	- 1.6
20-15	500	600	+20.0
20-24	270	340	+26.0
20-25	180	170	- 5.6

* See Table XXI and text.
** Using quartering sampling technique.

TABLE XXI

DISTRIBUTION OF Pb AS A FUNCTION OF PARTICLE SIZE ON SAMPLE #40-13

Screen Size (Mesh)	Percentage of Total Sample	ppm Pb
40-60	57.69	648
60-80	12.12	1424
80-100	4.69	15.31
< 100	25.50	2208

Another indication of the accuracy of the atomic absorption technique can be obtained by inspection of Table XXII. A soil sample was doped with different amounts of lead and then analyzed by both the AAS and emission techniques. Recovery is complete for both techniques within experimental error.

TABLE XXII

RECOVERY OF Pb FROM A SOIL SAMPLE BY AAS AND ES

Sample Description	Atomic Absorption		Emission Spectroscopy	
	ppm Pb Found	Percent Recovery*	ppm Pb Found	Percent Recovery*
Soil A	7	--	12	--
Soil A + 100 μg Pb	105	98.2	100	93.4
	110	104.5		
Soil A + 300 μg Pb	300	97.8		
	305	99.4		
Soil A + 600 μg Pb	600	98.7	590	97.2
	605	99.6	595	98.0
Soil A + 1000 μg Pb	995	99.3		
	1010	100.1		

* A residual concentration of 7 ppm was assumed to be correct.

Although the atomic absorption technique appears to provide precise data of high accuracy, one may raise the following philosophical question: Is it necessary to strive for 2% precision when analyzing populations which may show natural variations of 10-20%? Because of the large number of analyses that are required, the faster emission spectrographic method is generally preferred for soil samples.

4. Lead Compound Characterization

A series of extraction experiments with various solvents was carried out to determine roughly what types of lead compounds might be present in soil. A soil sample collected adjacent to the highway containing 1130 ppm total lead was used for the study. Each 10-gram sample was placed in a closed Teflon container with 100 ml of each solvent and allowed to equilibrate with shaking for 240 hours at room temperature. The solution was then filtered and analyzed for lead by AAS. Results are summarized in Table XXIII and indicate that the fraction of lead compounds which is soluble in organic solvents is quite small.

TABLE XXIII

SOLVENT EXTRACTION OF LEAD FROM SOIL

Solvent	Solubility µg/ml	% of Total Amount Present in Soil
Distilled Water	0.8	0.07
3 M HNO_3	1110	99.9
Ethyl Alcohol	0.13	0.01
Acetone	1.1	0.10
Sec. Butanol	1.4	0.12
Methyl Isobutyl Ketone	1.3	0.11
Toluene	13.	1.1

C. Air Filter Analysis

Lead blanks for air filters are of major concern due to the stringent requirement of short air sampling times. Results of a number of lead determinations for 8x10-inch glass-fiber filters are given in Table XXIV. The average lead blank was found to be 39 μg per filter with a relative standard deviation of ±49%. Use of glass-fiber filters was subsequently abandoned for short atmospheric sampling periods.

TABLE XXIV

Pb CONTENT OF 8x10-INCH GLASS-FIBER FILTERS

Filter Batch	Replicate #	μg Pb/Filter
A	1	40
	2	30
B	1	13
C	1	65
	2	65
D	1	29
	2	32
	Average	39

Several extraction methods for removing lead from air filters were investigated. Results of extraction by wet digestion and dry ashing are given in Table XXV. For purposes of comparison, each filter is split into sections of comparable size, and each section is then analyzed separately. Comparison of wet digestion and dry ashing techniques indicates that reproducibility of the wet digestion method is quite good. However, considerable lead loss occurs using the 450°C ashing technique.

TABLE XXV

COMPARISON OF DRY ASHING VS. WET DIGESTION ON GLASS-FIBER FILTER SAMPLES

		µg Pb/2 sq. in.	
Sample #	Section #	Wet Digestion	Dry Ashing
A	1	18.4	3.0
	2	17.1	6.6
	3	18.6	2.2
	4	17.3	5.9
	Average	17.9±4.2%	4.4±49%
	Loss due to ashing	75.3%	
B	1	3.8	3.2
	2	3.9	3.6
	3	3.8	3.2
	Average	3.8±1.6%	3.35±7.2%
	Loss due to ashing	11.8%	
C	1	12.7	11.4
	2	13,4	8.3
	3	14.4	10.7
	Average	13.5±6.3%	10.1±16%
	Loss due to ashing	25.2%	

1. Effect of Silica

We have fo[illegible] that the presence of silica in samples can lead to low atomic absorption values for lead. The time-dependence of this effect is shown in Figure 42. This problem is circumvented by maintaining an acid concentration of 3 or more as shown in Figure 43. This procedure has therefore been adopted as standard practice in atomic absorption analysis for lead. The atomic absorption procedure adopted for air filter analysis is essentially identical to that used for soil. Background correction is necessary in both cases.

EFFECTS OF TIME AND HNO_3 CONCENTRATION ON AAS LEAD DETERMINATION

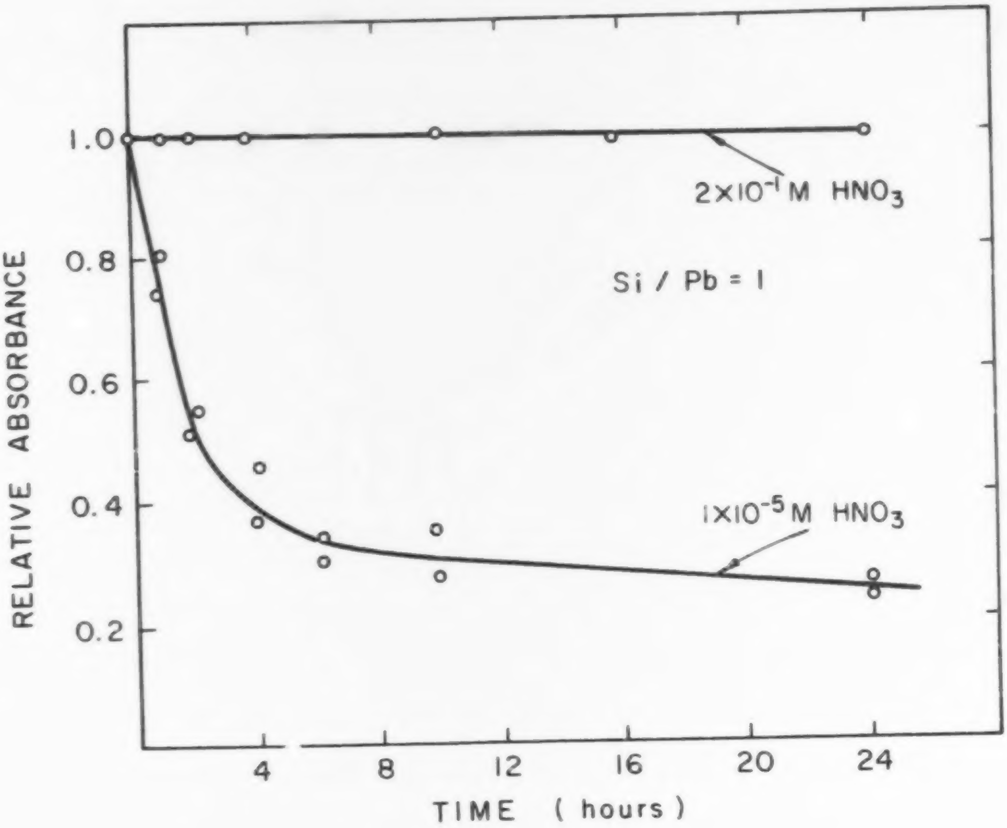


Figure 42

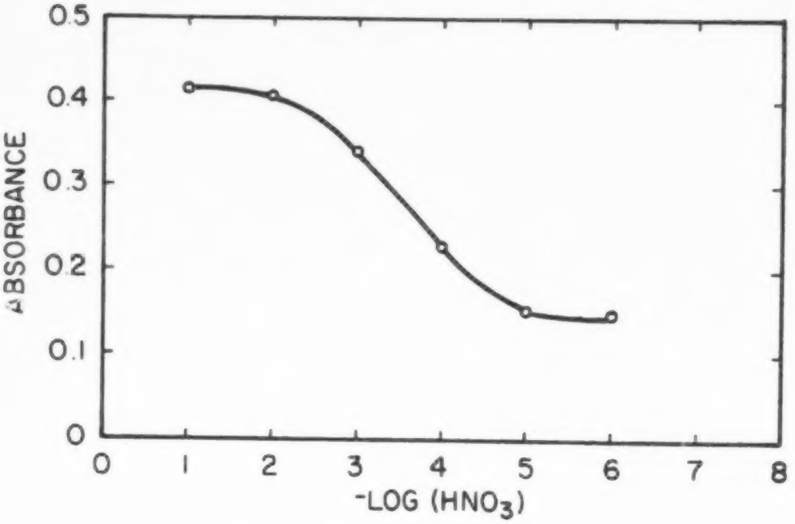

EFFECT OF HNO_3 CONCENTRATION ON AAS LEAD DETERMINATION

Figure 43

2. Volatilization of Lead

Possible loss of lead on filters through volatilization during storage was investigated. Mechanisms postulated were loss through volatilization of lead compounds having appreciable vapor pressure and photochemical decomposition. Filters upon which atmospheric lead had been collected with high-volume samplers were obtained for this study. The filters were cut into two-square-inch sections upon receipt in the laboratory, and replicate sections were analyzed immediately. The remaining sections were stored, half in light and half in dark. The analytical results are shown in Table XXVI. While some trend is apparent for the light-stored filters of Set A, differences are not significant at the 95% confidence level. It must therefore be concluded that differences arise from random variations among filter sections and not from a loss of lead. Results for Set B verify this explanation.

TABLE XXVI

LEAD CONTENT OF FILTERS ON STORAGE, $\mu g/in^2$

Elapsed Time, Hours	Set A		Set B	
	Light stored	Dark stored	Light stored	Dark stored
0			19.5±1.4	19.5±1.4
½			17.4	---
1	0.82±0.10	0.82±0.10	18.0	16.3
2	0.42	0.68	16.9	18.4
4	----	0.78	17.5	17.1
8	0.35	0.76	17.3	17.1
16	0.53	0.76		
32	0.51	0.78		
64	0.53	0.74		
128	0.62	0.64		
256	1.05(?)	---		
Average	0.54±0.15	0.74±0.06	17.4±0.4	17.2±0.9

The attempt was also made to remove lead collected on a filter under vacuum. A filter with a lead content of 0.66 $\mu g/in^2$ was pumped through a cold trap for 24 hours. Analysis of the pumped section gave a value of 0.64 $\mu g/in^2$ indicating no loss. A third section was purged with a stream of argon into a nitric acid scrubber for 24 hours. Analysis of the filter and the scrubber again indicated no loss. From these experiments we conclude that if loss occurs, it occurs before the filter arrives in the laboratory.

D. Biological Samples

Biological samples, e.g. plant and animal tissues, are analyzed by atomic absorption spectrometry. Samples are digested in hot HNO_3 with addition of sufficient $HClO_4$ to clarify the solution. Digests are diluted to volume with 3 molar HNO_3 and analyzed by AAS with background correction. The necessity for the background correction was mentioned previously and illustrated graphically in Figure 41. Unless the correction is made the results for a sample containing 1 μg Pb/ml will be high by a factor of three to four.

We have compared AAS analysis results for a set of samples with results obtained by the dithizone colorimetric method. These data are summarized in Table XXVII. Reproducibility of the colorimetric method as determined by analysis of standards is ±10%. Agreement of data in Table XXVII is therefore within expectations. Because the colorimetric technique involves a double extraction procedure and therefore considerable handling for sample preparation, the simpler, more precise atomic absorption method is preferred for biological samples.

TABLE XXVII

COMPARATIVE Pb ANALYSIS OF ORGANS BY AAS AND COLORIMETRY

Sample Identity	ppm AAS	ppm Colorimetry
Brain	43	46
Hair	5.6	4.6
Liver	3.7	3.6
Lung	11.5	13.8

E. Compound Identification

Attempts to identify the forms of lead in soil and air filter extracts by differential UV-visible and infrared spectrometry have not been successful due to the small amounts of lead present. Use of gas chromatography, mass spectrometry, and x-ray diffraction are presently being explored.

F. Isotope Ratio Analysis

Electrodeless discharge lamps for Pb^{204} and Pb^{206} isotopes have been obtained to evaluate determination of 204/206 ratios by atomic absorption. An isotope ratio mass spectrometer has been obtained by the Department of Chemistry and will soon be available for lead isotope ratio analyses. Determination of lead isotope ratios may be useful as a tracer technique (Ault, 1970; Nathans *et al.*, 1971).

XII. REFERENCES

Allen, R. R. and C. G. Gerhold, "Catalytic Converters for New and Current (Used) Vehicles," presented at the Fifth Technical Meeting, West Coast Section, Air Pollution Control Association, San Francisco, California, October 8-9, 1970.

Air Pollution Control Association, Preprints, Fifth Technical Meeting, West Coast Section, San Francisco, California, October 8-9, 1970.

Atkins, P. R., "Lead in a Suburban Environment," J. Air Poll. Control Assoc., 19, 591 (1969).

Ault, W. U., R. G. Senechal, and W. E. Erlebach, "Isotopic Composition as a Natural Tracer of Lead in the Environment," Environ. Sci. Technol., 4, 305 (1970).

Bazell, R. J., "Lead Poisoning: Zoo Animals May Be the First Victims," Science, 173, 130 (1971).

Bedrosian, A. J., R. K. Skogerboe, and G. H. Morrison, Anal. Chem., 40, 854 (1968).

Begeman, C. R., and J. M. Colucci, "Polynuclear Aromatic Hydrocarbon Emissions from Automotive Engines," presented at the Society of Automotive Engineers Meeting, Detroit, Michigan, May, 1970.

Besner, I. D. and P. R. Atkins, "The Dispersion of Lead and Carbon Monoxide from a Heavily Travelled Highway," Technical Report EHE-70-08, Dept. of Civil Engineering, The University of Texas at Austin, Austin, Texas, May, 1970.

Blemel, K. G., "Atmospheric Lead Concentrations as a Function of Meteorology," Arch. Environ. Health, 14, 594 (1967).

Bonner & Moore Associates, Inc., "An Economic Analysis of Proposed Schedules for Removal of Lead Additives from Gasoline," Environmental Protection Agency Contract No. 68-02-0050, Houston, Texas, 1971.

Cantwell, E. N., "A Total Exhaust Emission Control System," presented at the Air Pollution Control Association Meeting, Montbello, Quebec, Canada, September 20-22, 1970.

Charlson, R. J. and J. M. Pierrard, "Short Communication: Visibility and Lead," Atmos. Environ., 3, 479 (1969).

Chisolm, J. J., Jr., "Lead Poisoning," Sci. Amer., 224(2), 15 (1971).

Chow, T. J. and J. L. Earl, "Lead Aerosols in the Atmosphere: Increasing Concentrations," Science, 169, 577 (1970).

Craig, P. P. and E. Berlin, "The Air of Poverty," Environment, 13(5), 2 (1971).

Daines, R. H., H. Motto, and D. M. Chilko, "Lead in Soils and Plants: Its Relationship to Traffic Volume and Proximity to Highways," Environ. Sci. Technol., 4, 318 (1970).

Dedolph, R., G. Ter Haar, R. Holtzman, and H. Lucas, Jr., "Sources of Lead in Perennial Ryegrass and Radishes," Environ. Sci. Technol., 4, 217 (1970).

Department of Health, Education, and Welfare, "Survey of Lead in the Atmosphere of Three Urban Communities," Public Health Service Publication No. 999-AP-12, January, 1965.

Eccleston, B. and R. W. Hurn, "Comparative Emissions from Some Leaded and Prototype Lead-Free Automobile Fuels," U. S. Department of the Interior, Bureau of Mines Report of Investigations #7390, 1970.

Edwards, H. W., "Direct Determination of Silver in Air by Atomic Absorption Spectrometry," Anal. Chem., 41, 1172 (1969).

Felt, A. E. and R. V. Kerley, "Engines and Effects of Lead-Free Gasoline," presented at the Society of Automotive Engineers Mississippi Valley Section Meeting, Paper 710367, October 22, 1970.

Fuller, J. D., "The Economics of Refining and Lead's Part In It," Colorado State University Environmental Lead Project Seminar, Fort Collins, Colorado, September 28, 1971.

"Gasoline--Antipollution Forces Bring Marked Changes to Petroleum Refining Industry," Chem. Eng. News, November 9, 1970, p. 52-60.

Gilmore, J., "Policy Analysis: Response to Technological Threats," Colorado State University Environmental Lead Project Seminar, Fort Collins, Colorado, March 25, 1971.

Goldsmith, J. R., "Epidemiological Bases for Possible Air Quality Criteria for Lead," J. Air Poll. Control Assoc., 19, 714 (1969).

Golz, H. H., "Interim Report Observes Lead Levels in Air and Blood," J. Air Poll. Control Assoc,, 21, 455 (1971).

Grant, L. O. and R. F. Reinking, "On Air Pollutants as Ice Nuclei," presented at the American Meteorological Society Meeting, San Francisco, California, January, 1971.

Guinee, V. G., "Lead Poisoning in New York City," Trans. N.Y. Acad. Sci., 33(5), 539 (1971).

Habibi, K., "Characterization of Particulate Lead in Vehicle Exhaust--Experimental Techniques," Environ. Sci. Technol., 4, 239 (1970).

Habibi, K., E. S. Jacobs, W. G. Kunz, Jr., and D. L. Pastell, "Characterization and Control of Gaseous and Particulate Exhaust Emissions from Vehicles," presented at the Air Pollution Control Association Meeting, San Francisco, California, October 8-9, 1970.

Haley, T. J., "A Review of the Toxicology of Lead," Air Quality Monograph #69-7, American Petroleum Institute, 1969.

Hartman, L. M. and D. A. Seastone, "Economic Interdependencies and Water Use," in Water Research, A. Kneese and S. Smith, eds., Johns Hopkins, 1966.

Hirschler, D. A., L. F. Gilbert, F. W. Lamb, and L. M. Niebylski, "Particulate Lead Compounds in Automobile Exhaust Gas," Ind. Eng. Chem., 49, 1131 (1957).

Hirschler, D. A. and F. J. Marsee, "Meeting Future Automobile Emission Standards," presented at the National Petroleum Refiners Association Meeting, San Antonio, Texas, April 6-7, 1970.

Hunter, J., GM Research Laboratories paper presented at the Central States Section Meeting, Combustion Institute (J. Air Poll. Control Assoc., 21, 362 (1971)).

Hyman, M. H., "Timetable for Lead," Environment, 13, 4 (1971).

Inman, R. E., R. B. Ingersoll, and E. A. Levy, "Soil: A Natural Sink for Carbon Monoxide," Science, 172, 1229 (1971).

"Interdisciplinary Team Studies Impact of Lead," Chem. Eng. News, June 28, 1971, p. 25.

Jacobs, E. S., P. J. Brandt, C. S. Hoffman, Jr., G. H. Patterson, and R. L. Willis, "Polynuclear Aromatic Hydrocarbon Emission from Vehicles," presented at the American Chemical Society National Meeting, Los Angeles, California, March 31, 1971.

Julien, H. P. and R. E. Ogilvie, "High Temperature X-Ray Study of Lead

Halides and Oxyhalides," J. Am. Chem. Soc., 82, 293 (1960).

Konopinski, V. J. and J. B. Upham, "Commuter Exposure to Atmospheric Lead," Arch. Environ. Health, 14, 589 (1967).

LaBreque, M. L., "A Bill of Particulates," The Sciences, June-July, 1971, p. 16.

Lamb, F. W. and L. M. Niebylski, "Formation of Engine-Deposit Compounds by Solid-State Reactions," Anal. Chem., 23, 1388 (1951).

Landsberg, H. E., "Man-Made Climatic Changes," Science, 170, 1265 (1970).

Lazrus, A. L., E. Lorange, and J. P. Lodge, Jr., "Lead and Other Metal Ions in United States Precipitation," Environ. Sci. Technol., 4, 55 (1970).

"Lead Free Gas Feasible but Costly, UOP Says," Chem. Eng. News, January 12, 1970, p. 51.

"Lead in Gas Down," Chem. Eng. News, July 12, 1971, p. 13.

"Lead in Gasoline: What Would It Cost to Reduce or Eliminate?", Chemical Week, December 24, 1969, p. 71.

Leontief, W., Studies in the Structure of the American Economy, Oxford Press, New York, 1959.

Leontief, W., "Input-Output Economics," Sci. Amer., 185(4), 15 (1951).

Lindeken, C. L., F. K. Petrock, W. A. Phillips, and R. D. Taylor, "Surface Collection Efficiency of Large-Pore Membrane Filters," Health Physics, 10, 495 (1964).

Lininger, R. L., R. A. Duce, J. W. Winchester, and W. R. Matson, "Chlorine, Bromine, Iodine, and Lead in Aerosols from Cambridge, Massachusetts," J. Geophys. Research, 71, 2457 (1966).

Lutz, G. A., A. A. Levin, S. G. Bloom, K. L. Nielsen, J. L. Cross and

D. L. Morrison, "Final Report, Volume III. Lead Model Case Study," U.S. Dept. HEW, Contract #CPS-69-005, Battelle Memorial Institute, Columbus, Ohio, June, 1970.

Mason, B. J., Clouds, Rain and Rainmaking, University Press, Cambridge, Massachusetts, 1962.

Megaw, W. J. and R. D. Wiffen, "The Efficiency of Membrane Filters," Int. J. Air Wat. Poll., 7, 501 (1963).

Moran, J. B., O. J. Nanary, R. J. Herling, W. Karches, and J. Wagman, "The Nature of Automotive Aerosols," presented at the Division of Colloid and Surface Chemistry Meeting, American Chemical Society, Atlanta, Georgia, June 21-23, 1971.

Morgan, G. M., "The Production of Potential Ice Nuclei by Gasoline Engines," J. Appl. Meteorol., 7, 214 (1968).

Morgan, G. M., "Technique for Detecting Lead Particles in Air," Nature 213, 58 (1967).

Motto, H. L., R. H. Daines, D. M. Chilko, and C. K. Motto, "Lead in Soils and Plants: Its Relationship to Traffic Volume and Proximity to Highways," Environ. Sci. Technol., 4, 231 (1970).

Mueller, P. K., H. L. Helwig, A. E. Alcocer, W. K. Gong, and E. E. Jones, "Concentration of Fine Particles and Lead in Car Exhaust," ASTM Special Technical Publication No. 352, 1963, p. 60-73.

Murozumi, M., T. J. Chow, and C. C. Patterson, "Chemical Concentrations of Pollutant Lead Aerosols, Terrestrial Dusts and Sea Salts in Greenland and Antarctic Snow Strata," Geochim. Cosmochim. Acta, 33, 1247 (1969).

Nathans, M. W. and G. J. Stopps, "Global Effects of Lead-Containing Pollutants," presented at the Air Pollution Control Association 64th Annual Meeting, Atlantic City, New Jersey, June 27-July 2, 1971.

"National Air Quality Standards," J. Air Poll. Control Assoc., 21, 352 (1971).

"National Air Quality Standards Finalized," Environ. Sci. Technol., 5, 503 (1971).

Ogden, D. C. "Economic Analysis of Air Pollution," Land Economics, May, 1966.

Olin, J. G., G. J. Sem, and R. P. Trautner, "Air-Quality Monitoring of Particle Mass Concentration with a Piezoelectric Particle Microbalance," presented at the Air Pollution Control Association 64th Annual Meeting, Atlantic City, New Jersey, June 27-July 2, 1971.

Pasquill, F., Atmospheric Diffusion, D. Van Nostrand Co. Ltd., London, 1962.

Patten, B. C., Systems Analysis and Simulation in Ecology, Vol. I., Academic Press, New York, 1971.

Pierrard, J. M. and R. A. Crane, "The Effect of Gasoline Compositional Changes on Atmospheric Visibility and Soiling," presented at the Air Pollution Control Association 64th Annual Meeting, Atlantic City, New Jersey, June 27-July 2, 1971.

Reiter, E. R., "A Case Study of Radioactive Fallout," J. Appl. Meteorol., 2, 691 (1963).

Reiter, E. R., "Further Studies on Radioactive Fallout," Colorado State University Atmospheric Science Paper No. 70, COO-1340-6, 1965.

Robinson, E., F. L. Ludwig, J. E. DeVries, and T. E. Hopkins, "Variations of Atmospheric Lead Concentrations and Type with Particle Size," Stanford Research Institute Project No. PA-4211, 1963.

SCEP Group, Man's Impact on the Global Environment-Assessment and Recommendations for Action, The MIT Press, Cambridge, Massachusetts, 1970.

Schaefer, V. J., "Ice Nuclei from Automobile Exhaust and Iodine Vapor," Science, 154, 1555 (1966).

Schaefer, V. J., "Ice Nuclei from Auto Exhaust and Organic Vapors," J. Appl. Meteorol., 7, 148 (1968).

Schaefer, V. J., "The Inadvertent Modification of the Atmosphere by Air Pollution," Bull. Amer. Meteorol. Soc., 50, 199 (1969).

Schaefer, V. J., "Auto Exhaust, Pollution, and Weather Patterns," Bull. Atomic Scientists, October, 1970, p. 31-33.

Schroeder, H. A. and I. Tipton, "The Human Body Burden of Lead," Arch. Environ. Health., 17, 965 (1968).

Schuck, E. A. and J. K. Locke, "Relationship of Lead Particulates to Certain Consumer Crops," Environ. Sci. Technol., 4, 324 (1970).

Slade, D. H., ed., Meteorology and Atomic Energy, U. S. Atomic Energy Commission, TID-24190, 1968, Sections 3 & 4 of Chapter 5.

"Substitutes for Lead Antiknocks Few and Far Between," Environ. Sci. Technol., 5, 487 (1971).

Sutton, O. G., Atmospheric Turbulence, Methuen & Co., Ltd., London, 1959, ch. 5.

Swartzman, G., Some Concepts of Modeling, USIBP Grassland Biome Technical Report No. 32, 142 p., 1970.

Taliaferro, H. R., L. T. Wright, and R. C. Mallat, "Gasoline for Reducing Automobile Pollution," presented at the American Association for the Advancement of Science 137th Meeting, Chicago, Illinois, December 27, 1970.

"TEL Complement," Chem. Eng. News, June 14, 1971, p. 19.

Ter Haar, G. L., "Air As a Source of Lead in Edible Crops," Environ. Sci. Technol., 4, 226 (1970).

Ter Haar, G. L., "The Effect of Lead Antiknocks on the Lead Content of Crops," presented at the Washington Academy of Sciences Meeting, Washington, D.C., 1971.

Thomas, H. V., B. K. Miomore, G. A. Heibreder, and B. A. Kogan, "Blood Lead of Persons Living Near Freeways," Arch. Environ. Health, 15, 645 (1967).

"Toyo Ethyl, K.K., has canceled startup of Japan's first lead alkylates plant," Chem. Eng. News, January 18, 1971, p. 16.

Van Dyne, G. N., Analysis of Structure, Function, and Utilization of Grassland Ecosystems, A Progress Report and Continuation Proposal, Colorado State University, Fort Collins, Colorado, 1971.